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**Sixth Symposium on Chemical Evolution and the Origin
and Evolution of Life**

Sara E. Acevedo, Donald L. DeVincenzi, and Sherwood Chang, Editors

National Aeronautics and
Space Administration

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PREFACE

This report contains session summaries and abstracts from the Sixth Symposium on Chemical Evolution and the Origin and Evolution of Life, organized on behalf of NASA's Exobiology Program and held November 17-20, 1997 at NASA's Ames Research Center, Moffett Field, California.

The Exobiology Program is a key element of NASA's nascent Astrobiology Initiative; "Astrobiology is defined as the study of life in the universe, and the chemical and physical forces and adaptations that influences life's origins, evolution, and destiny."

The goal of NASA's Exobiology Program is to understand the origin, evolution, and distribution of life in the universe. The Exobiology Program is therefore quite broad in scope and subject areas covered during the Symposium included: Cosmic Evolution of the Biogenic Compounds, Prebiotic Evolution, Early Evolution of Life, Evolution of Advanced Life, and Space Exploration For Exobiology.

The Symposium provided an opportunity for NASA's Exobiology principal investigators to present their most recent research results. In addition, the symposium helped foster increased communication across disciplinary lines, formulate a more integrated program approach, review progress in all tasks, and increase visibility of the Exobiology Program.

The more than 200 participants included Exobiology grantees, NASA Ames Research Center staff, graduate students, and invited guests. Current plans are to continue to schedule this symposium every three years. Further information about NASA's Exobiology Program can be found at:

http://exobiology.nasa.gov/Exobiology_Program/program.html

Michael Meyer
Astrobiology Discipline Scientist
NASA Headquarters

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* The abstracts for the oral presentations appear in order of presentation. The page number for any individual abstract can be found by the speaker's name in the *Speaker's Index* at the back of this document.

AGENDA

----- MONDAY NOVEMBER 17, 1997 -----

SYMPOSIUM SESSION I (OPENING REMARKS)

- 8:30 am Introduction & Logistics (Donald DeVincenzi and Sara Acevedo)
8:40 am Welcome (Henry McDonald)
8:50 am Astrobiology & Exobiology (Michael Meyer)

SYMPOSIUM SESSION II Co-Chairs: J. Farmer and D. Deamer

- 9:10 am INFRARED CAVITY RINGDOWN LASER ABSORPTION SPECTROSCOPY OF CARBON CLUSTERS
(Robert Provencal, Joshua Paul, and Richard Saykally*)
- 9:30 am HYDROGENATED PAH (AN AROMATIC & ALIPHATIC SPECIES) AS A COMPONENT OF THE INTERSTELLAR AND CIRCUMSTELLAR MEDIUMS
(Thomas J. Wdowiak*, Kenneth M. Arnoult, and Luther W. Beegle)
- 9:50 am IDENTIFICATION OF ORGANIC CARBON IN INTERPLANETARY DUST
(G.J. Flynn*, L.P. Keller, and M.A. Miller)
- 10:10 am ADDITIONAL EVIDENCE FOR POSSIBLE BIOGENIC ACTIVITY IN THE MARTIAN METEORITE ALH84001
(D.S. McKay*, E.K. Gibson, K. Thomas-Keptra, and C.S. Romanek)
- 10:30 am Coffee Break
- 10:50 am THE SEARCH FOR LIFE ON MARS
(John F. Kerridge*)
- 11:10 am RADAR DETECTABILITY OF A SUBSURFACE OCEAN ON EUROPA
(Christopher F. Chyba*)
- 11:30 am EARLY LIFE ENVIRONMENTS ON EARTH AND MARS (ELEEM)
(G. Arrhenius, S.J. Mojzsis*, T.M. Harrison, K.D. McKeegan, A.P. Nutman, and C.R.L. Friend)
- 11:50 am *IN VITRO* EVOLUTION OF NOVEL RNA AND DNA ENZYMES
(Gerald F. Joyce*, Martin C. Wright, and Richard K. Bruick)
- 12:10 pm Lunch Break

* speaker; to find the abstract of a particular presentation, check the Speakers' Index at the back of this report for the page number.

SYMPOSIUM SESSION III
Co-Chairs: Y. Pendleton and D. Lies

- 1:30 pm CHEMISTRY OF THE BIOGENIC ELEMENTS IN DENSE INTERSTELLAR CLOUDS AND RELATIONS TO THE SOLAR SYSTEM
(W.M. Irvine and J.E. Dickens*)
- 1:50 pm PHOTOCHEMICAL EVOLUTION OF THE BIOGENIC ELEMENTS IN PRE-COMETARY/INTERSTELLAR ICE ANALOGS
(L.J. Allamandola*)
- 2:10 pm IS MOTHER EARTH THE MOTHER OF LIFE? THE SEARCH FOR ORGANIC MOLECULES INSIDE MINERALS AND ROCKS
(Friedemann Freund* and Alka Gupta)
- 2:30 pm MOLECULAR MODELING OF PROTOCELLULAR STRUCTURES AND FUNCTIONS
(Andrew Pohorille*, Michael A. Wilson, Michael H. New, and Christopher Chipot)
- 2:50 pm STRUCTURE AND FUNCTION OF ENCAPSULATED REPLICATING SYSTEMS
(David W. Deamer*)
- 3:10 pm Coffee Break
- 3:30 pm PHOTOSYNTHESIS AND IRON IN HIGH IRON MICROBIAL MATS
(Beverly K. Pierson*)
- 3:50 pm SPECIES COMPOSITION OF HOT SPRING CYANOBACTERIAL MATS
(David M. Ward* and Thane Papke)
- 4:10 pm BIOGEOCHEMISTRY OF CARBON IN THE ANCIENT BIOSPHERE: PERSPECTIVES FROM MODERN MICROBIAL COMMUNITIES AND THE ANCIENT CARBON ISOTOPIC RECORD
(David J. DesMarais*, A. Tharpe, and J. Thompson)
- 4:30 pm THE DISTRIBUTION OF PROTEROZOIC FOSSILS IN TIME AND SPACE
(Andrew H. Knoll*)
- 4:50 pm THE BIOLOGICAL POTENTIAL OF MARS (AND MARS MISSIONS)
(Bruce Jakosky*)
- 5:10 pm Adjourm for the day

----- TUESDAY NOVEMBER 18, 1997 -----

SYMPOSIUM SESSION IV
Co-Chairs: L. Allamandola and B. Pierson

- 8:30 am THE NASA SPECIALIZED CENTER OF RESEARCH AND TRAINING (NSCORT) IN EXOBIOLOGY
(Jeffrey L. Bada*, Stanley L. Miller, Gustaf Arrhenius, Russell F. Doolittle, Christopher Wills, Gerald Joyce, and Leslie Orgel)

- 8:50 am ENANTIOMERIC EXCESSES IN THE AMINO ACIDS OF CARBONACEOUS CHONDRITES
(John Cronin* and Sandra Pizzarello)
- 9:10 am MODIFICATION OF AMINO ACIDS AT SHOCK PRESSURES OF 3.5 TO 32 GPa
(Etta Peterson, Friedrich Horz, George Cooper, and Sherwood Chang*)
- 9:30 am AN INVESTIGATION OF SUGARS AND OTHER POSSIBLE FORMALDEHYDE PRODUCTS IN THE MURCHISON METEORITE
(George Cooper*)
- 9:50 am CO-ORIGIN OF METABOLISM AND BIOPOLYMER SYNTHESIS USING FORMOSE SUGAR SUBSTRATES
(Arthur L. Weber*)
- 10:10 am Coffee Break
- 10:30 am THE ORIGIN AND EVOLUTION OF OXYGENIC PHOTOSYNTHESIS
(Robert E. Blankenship* and Hyman Hartman)
- 10:50 am HORIZONTAL GENE TRANSFER: PITFALLS AND PROMISES
(J. Peter Gogarten*, Elena Hilario, and Lorraine Olendzenski)
- 11:10 am GENES AND ENZYMES OF ANAEROBIC METABOLISM IN SHEWANELLA PUTREFACIENS
(Kenneth H. Nealson, Doug Lies*, Sasha Tsapin, and James Scott)
- 11:30 am VIABLE BACTERIA IN SIBERIAN AND ANTARCTIC PERMAFROST
(E.I. Friedmann*, A.D. Gilichinsky, T. Shi, G.S. Wilson, R.H. Reeves, V.E. Ostroumov, E.A. Vorobyova, V.S. Soina, V.A. Shcherbakova, T.A. Vishnivetskaya, J.P. Chanton, R.O. Friedmann, C.P. McKay, and E.M. Rivkina)
- 11:50 am POLAR ANALOGS TO MARS
(C. McKay*, D. Andersen, W. Davis, and E.I. Friedmann)
- 12:10 am Lunch Break

SYMPOSIUM SESSION V
Co-Chairs: S. Cady and C. Chyba

- 1:30 pm THE END PERMIAN MASS EXTINCTION: GEOCHRONOLOGY AND PATTERNS OF EXTINCTION
(Douglas H. Erwin*, Samuel A. Bowring, Mark Martin, Kathy Davidek, and Jin Yugan)
- 1:50 pm ORDOVICIAN BIODIVERSITY: GEOGRAPHY AND ENVIRONMENT
(Arnold I. Miller*)
- 2:10 pm WAS HIGH OBLIQUITY THE CAUSE OF LOW-LATITUDE PRECAMBRIAN GLACIATION?
(Darren M. Williams*, James F. Kasting, and Lawrence Frekes)

- 2:30 pm PALEOBIOLOGY OF THE TERMINAL PROTEROZOIC: PRELUDE TO THE
CAMBRIAN EXPLOSION
(Bruce Runnegar*)
- 2:50 pm CO₂ GREENHOUSE IN THE EARLY MARTIAN ATMOSPHERE: SO₂ INHIBITS
CONDENSATION
(Y.L. Yung*, H. Nair, and M.F. Gerstell)
- 3:10 pm Coffee Break
- 3:30 pm DIFFUSION OF PHOTOCHEMICALLY PRODUCED HYDROGEN PEROXIDE IN THE
MARTIAN REGOLITH
(Richard C. Quinn and Aaron P. Zent*)
- 3:50 pm THE SUDBURY IMPACT CRATER: EFFECTS ON CARBONACEOUS MATTER
(T.E. Bunch*, L. Becker, J. Bada, D. Glavin, D. Des Marais, P. Schultz, F. Rietmeijer,
and W. Wolbach)
- 4:10 pm METEORITE IMPACT PRODUCTION OF VOLATILES AND THEIR BIOSPHERIC
EFFECTS AT THE CRETACEOUS/TERTIARY BOUNDARY
(Kevin O. Pope*, Kevin H. Baines, and Adriana C. Ocampo)
- 4:30 pm SHOCK SYNTHESIS OF ORGANICS IN COMETARY IMPACTS
(C.P. McKay* and B. Borucki)
- 4:50 pm DEVELOPMENT OF A LASER RAMAN SPECTROMETER FOR IN SITU
EXOBIOLGY EXPLORATION
(Thomas J. Wdowiak*, David G. Agresti, Sergey B. Mirov, and Anatoly B. Kudryavtsev)
- 5:10 pm Adjourn for the day

----- WEDNESDAY NOVEMBER 19, 1997 -----

SYMPOSIUM SESSION VI
Co-Chairs: T. Kanavarioti and D. Lowe

- 8:30 am NON-ENZYMATIC OLIGOMERIZATION OF MONONUCLEOTIDES USING
NON-STANDARD OLIGONUCLEOTIDE TEMPLATES
(Christopher Switzer*, Thazha P. Prakash, Rajanikanth Bandaru, Christopher
Roberts, and John Chaput)
- 8:50 am TEMPLATE-DIRECTED SYNTHESIS OF DNA-PNA CHIMERAS
(Leslie E. Orgel* and Marcus Koppitz)
- 9:10 am TITAN HAZE: CYANOACETYLENE AND CYANOACETYLENE-ACETYLENE
PHOTOPOLYMERS
(James P. Ferris* and David Clarke)
- 9:30 am ABIOTIC ORGANIC SYNTHESIS UNDER SIMULATED HYDROTHERMAL
CONDITIONS
(Bernd R.T. Simoneit*, T.M. McCollum, and G. Ritter)

- 9:50 am HYDROTHERMAL ECOSYSTEMS IN A PLANETARY CONTEXT
(Everett L. Shock* and William B. McKinnon)
- 10:10 am Coffee Break
- 10:30 am ANOXIA AND EVOLUTIONARY PATTERNS IN THE SEA: ON-SHORE/OFF-SHORE
TRENDS AND RECENT RECRUITMENT OF THE DEEP-SEA AND
HYDROTHERMAL VENT FAUNAS
(David K. Jacobs* and David R. Lindberg)
- 10:50 am MÖSSBAUER SIGNATURES THAT MAY BE USEFUL IN IDENTIFYING RESIDUES
OF ANCIENT MARTIAN HYDROTHERMAL SYSTEMS
(Thomas J. Wdowiak*, David G. Agresti, Manson L. Wade, Lawrence P. Amendarez,
and Jack D. Farmer)
- 11:10 am EXPLORATION OF MONO LAKE USING TROV: APPLICATION OF
TELEPRESENCE TECHNOLOGY TO EXOBIOLOGY STUDIES
(C.R. Stoker*)
- 11:30 am RECOGNIZING BIOGENIC SIGNATURES NEAR LIFE'S UPPER TEMPERATURE
LIMIT THE ROLE OF HYPERTHERMOPHILIC BIOFILMS IN SPICULAR GEYSERITE
MORPHOGENESIS
(Sherry L. Cady*, David J. Des Marais, Jack D. Farmer, Malcolm R. Walter, Carrine E.
Blank, and Norman R. Pace)
- 11:50 am FOSSILIZATION PROCESSES IN THERMAL SPRINGS: COMPARATIVE STUDIES
OF MODERN AND ANCIENT SILICEOUS SPRING SYSTEMS
(Jack Farmer*, Brad Bebout, Linda Jahnke, David Des Marais, and Malcolm Walter)
- 12:10 am Lunch Break

SYMPOSIUM SESSION VII
Co-Chairs: L.P. Knauth and A. Weber

- 1:30 pm THE IKIRYU SINTER (500,000-300,000 YRS.), KYUSHU, JAPAN
(Donald R. Lowe* and Eiji Izawa)
- 1:50 pm PRESERVATION OF HALOARCHAEA AND THEIR MACROMOLECULAR
CONSTITUENTS IN BRINE INCLUSIONS FROM BEDDED SALT DEPOSITS
(J.K. Fredrickson*, T.C. Onstott, T.J. Bailey, and D.P. Chandler)
- 2:10 pm EXPOSURE OF OSMOPHILIC MICROBES TO THE SPACE ENVIRONMENT ON
BIOPAN: UV-RADIATION, THE EFFECT OF ANHYDROBIOSIS AND PROTECTION
MECHANISMS
(R.L. Mancinelli* and M.R. White)
- 2:30 pm THE ORIGINS OF THE TRANSLATION MACHINERY
(Deana C. Larkin, Susan A. Martinis, and George E. Fox*)
- 2:50 pm THE CASE AGAINST COMETARY ORIGIN OF THE OCEANS
(K.J. Zahnle*)
- 3:10 pm Coffee Break

- 3:30 pm ORGANICS IN SPACE: FROM STARDUST TO PLANETESIMALS
(Y. Pendleton*)
- 3:50 pm INTERSTELLAR PRECURSORS OF METEORITIC ORGANIC MOLECULES
(S.B. Charnley*)
- 4:10 pm WHAT BIOPOLYMERS ARE EXPECTED IN EXTRATERRESTRIAL
ENVIRONMENTS
(S.A. Benner*)
- 4:30 pm TOWARD RNA - THE MINERAL INDUCED PHOSPHORYLATION OF
GLYCOALDEHYDE
(G. Arrhenius, R. Krishnamurthy*, and S. Pitsch)
- 4:50 pm MARS SAMPLE RETURN QUARANTINE PROTOCOL WORKSHOP
(Donald L. DeVincenzi*)
- 5:10 pm PLANETARY PROTECTION AND MARS SAMPLE RETURN: FROM NOW
THROUGH LAUNCH AND BEYOND
(Margaret S. Race*)
- 5:30 pm Adjourn for the day
- 6:00 pm Poster Session

----- THURSDAY NOVEMBER 20, 1997 -----

SYMPOSIUM SESSION VIII
Co-Chairs: T. Wdowiak and L. Jahnke

- 8:30 am THE ABUNDANCE OF ^{13}C IN MARINE ORGANIC MATTER AND ISOTOPIC
FRACTIONATION IN THE GLOBAL BIOGEOCHEMICAL CYCLE OF CARBON
DURING THE PAST 800 MA
(John M. Hayes*, Harald Strauss, and A.J. Kaufman)
- 8:50 am MOLECULAR BIOMARKERS FOR CYANOBACTERIA
(Linda L. Jahnke*, Roger E. Summons, and Harold P. Klein)
- 9:10 am THE MARTIAN CARBON CYCLE AND IMPLICATIONS FOR THE $\delta^{13}\text{C}$ VALUE OF
THE ATMOSPHERE
(David Kass* and Yuk Yung)
- 9:30 am DETECTION, FORMATION, AND EVOLUTION OF COMPLEX HYDROCARBONS IN
PROTOSTELLAR CORES
(Thangasamy Velusamy*, William D. Langer, and Steven Levin)
- 9:50 am ANALYSIS OF THE CARBONACEOUS COMPONENT OF COMET HALLEY DUST
(Marina N. Fomenkova* and Sherwood Chang)
- 10:10 am Coffee Break

- 10:30 am THE STRUCTURE OF EXTRATERRESTRIAL WATER ICE
(David Blake*, Peter Jenniskens, and Lance Delzeit)
- 10:50 am THE MECHANISM OF AMINE-CATALYZED HYDROLYSIS OF RNA
(David A. Usher* and John R. Townsend)
- 11:10 am INORGANIC SOLIDS AND THE ORIGINS OF LIFE
(Paul S. Braterman*, Kevin Shannon, and Joseph Boclair)
- 11:30 am THE CHEMISTRY, MINERALOGY, AND SPECTROSCOPY OF THE BIOGENIC
ELEMENTS IN MARS SOIL ANALOGS
(J. Orenberg*, A. Banin, T. Rousch, and S. White)
- 11:50 am EARLY EVOLUTION OF LIFE IN NON-MARINE ENVIRONMENTS
(L. Paul Knauth*)
- 12:10 am Lunch Break

SYMPOSIUM SESSION IX
Co-Chairs: T. Bunch and J. Orenberg

- 1:30 pm THE DIVERSITY OF THE OUTER PLANETARY SYSTEM
(H. Levison* and J. Lissauer)
- 1:50 pm FORMATION OF THE ASTEROID BELT
(George W. Wetherill*, Stephen Kortenkamp, and John E. Chambers)
- 2:10 pm THE ROUTE FROM INTERSTELLAR TO PROTOSTELLAR ABUNDANCES:
EVIDENCE OF VARIABILITY IN THE INTERSTELLAR MEDIUM
(P. Wannier*, P. Schloerb, and G. Moriarty-Schieven)
- 2:30 pm SPECTROSCOPIC STUDIES OF PRE-BIOTIC CARBON CHEMISTRY
(Geoffrey A. Blake*)
- 2:50 pm THEORETICAL STUDIES OF THE EXTRATERRESTRIAL CHEMISTRY OF
BIOGENIC ELEMENTS AND COMPOUNDS
(David E. Woon*)
- 3:10 pm Coffee Break
- 3:30 pm REDUCED NITROGEN ON THE EARLY EARTH
(D.P. Summers and N. Lerner*)
- 3:50 pm PREFERENCE FOR INTERNUCLEOTIDE LINKAGES AS A FUNCTION OF THE
NUMBER OF CONSTITUENTS IN A MIXTURE
(Anastassia Kanavarioti*)
- 4:10 pm INTERACTIONS OF CARBON COMPOUNDS AND PHOSPHATE WITH PYRITE IN
AQUEOUS SOLUTIONS
(Martin Schoonen* and Joakim Bebie)
- 4:30 pm THE MEENTHEENA CARBONATE, ANCIENT LAKES, FACIES, AND EXO BIOLOGY
(Stanley M. Awramik* and H. Paul Buchheim)

4:50 pm MARS STUDIES
(H.P. Klein*)

5:10 pm Adjourn Symposium

----- POSTERS -----

IGNEOUS ROCKS THAT SPARKLE, CRACKLE AND GLOW OXIDIZING RADICALS ACTIVATED BY LOW VELOCITY IMPACTS (Jerome G. Borucki*, Steven J. Butow, Marshall Lisé, and Friedemann Freund)

FAMILY CALONYMPHIDAE: TERMITE PROTISTS RELEVANT TO EARLY EUKARYOTIC EVOLUTION (Michael Dolan and Lynn Margulis*)

HYDROTHERMAL PROSPECTING ON MARS (Jack D. Farmer*)

ORGANIC CARBON ASSOCIATED WITH CARBONATE IN ALH84001 (G.J. Flynn*, L.P. Keller, and M.A. Miller)

THE EFFECTS OF AMONG SITE RATE VARIATION ON PHYLOGENETIC RECONSTRUCTION FROM AMINO ACID SEQUENCES (J. Peter Gogarten* and Olga Zhaxybayeva)

ABUNDANT VIRUSES IN ANTARCTIC LAKES (Ray Kepner* and Bob Wharton)

EFFECT OF LEAVING GROUP ON THE DIMERIZATION OF PHOSPHOIMIDAZOLIDE-ACTIVATED NUCLEOTIDES (Lynn F. Lee* and Anastassia Kanavarioti)

HORIZONTAL GENE TRANSFER OF ARCHAEOAL GENES INTO THE DEINOCOCCACEAE (Ryan Murphy, Lorraine Olendzenski, Scott MacNamara, and J. Peter Gogarten*)

CHICXULUB IMPACT EJECTA IN BELIZE: INSIGHTS INTO THE ROLE OF ATMOSPHERES AND VOLATILES IN LARGE IMPACTS (Adriana C. Ocampo*, Kevin O. Pope, Alfred G. Fischer, and John R. Marshall)

THE PHYLOGENETIC POSITION OF THE MICROSPORIDIA: DEATH OF AN EARLY BRANCHING LINEAGE? (Lorraine Olendzenski, Elena Hilarío, and J. Peter Gogarten*)

METABOLIC ACTIVITY OF MICROORGANISMS IN PERMAFROST (E.M. Rivkina, E.I. Friedmann*, C.P. McKay, and A.D. Gilichinsky)

WHAT ARE THE CARRIERS OF THE UIRS? SINGLE PHOTON INFRARED EMISSION SPECTROSCOPY (SPIRES) OF UV-EXCITED PAHs (D.R. Wagner, D.J. Cook, and R.J. Saykally*)

STABLE CARBON ISOTOPE COMPOSITION OF CYANOBACTERIAL AND *CHLOROFLEXUS* BIOMARKERS IN HOT SPRING MATS CONSTRUCTED BY OXYGENIC AND/OR ANOXYGENIC PHOTOTROPHS (David M. Ward*, Marcel van der Meer, and Jan de Leeuw)

MARTIAN PALEOLAKE SEDIMENTS AND TERRESTRIAL ANALOGS: EXTANT AND EXTINCT ICE-COVERED LAKES (Robert A. Wharton Jr.* and Peter T. Doran)

THE OXIDATIVE STRATIGRAPHY OF THE MARTIAN REGOLITH (Aaron Zent*)

SESSION SUMMARIES

The following summaries were compiled by the co-chairs of each session. Individual abstracts from each paper or poster presented can be found in subsequent sections of this report.

SESSION I

Welcome and Opening Remarks

The Symposium opened with the welcome address by Michael Meyer, NASA's Astrobiology Discipline Scientist, who discussed the relationship between the extant exobiology program and NASA's nascent endeavor in Astrobiology.

The Exobiology Program is a key element of the Astrobiology Initiative, as "Astrobiology is defined as the study of life in the universe, and the chemical and physical forces and adaptations that influences life's origins, evolution, and destiny."

SESSION II

D. Deamer and J. Farmer, Co-Chairs

The carbon chemistry of interstellar space provides potentially important information about the nature of prebiotic chemical processes and their role in the nucleation of solid materials. R. Provencal (UC Berkeley) et al. discussed the results of an astrophysical study to evaluate the importance of previously unstudied pure carbon clusters in the interstellar environment using infrared diode laser absorption spectroscopy. With this technique they were able to characterize the structure, bonding, and other properties for carbon clusters containing as many as 13 carbon atoms. They supplemented their IR diode laser observations with far infrared measurements (10-200 cm^{-1}) to help design astronomical searches for SOPHIA (and previously for the Kuiper Airborne Observatory). A new technique called "cavity ringdown detection" was also developed for measuring infrared spectra of carbon clusters. This method permits the measurement of very small absorption features at Doppler-limited precision over the entire mid-IR.

T. Wdowiak (Univ. Alabama, Birmingham) et al. reported on the astronomical importance of polycyclic aromatic hydrocarbons (PAHs) in interstellar and circumstellar environments. Previous studies have focused on the importance of large aromatic carbon structures thought to explain emission bands in unidentified infrared (UIR) spectra. However, based on a 2175 angstrom extinction feature, it now appears that some fraction of the multi-ring structures in these environments could also include aliphatic compounds. The aliphatic/cycloalkane fraction of large hydrogenated PAHs can undergo cracking to form small chains, or be polymerized into kerogen-like structures similar to those found in carbonaceous chondrites. Thus, the aliphatic component of PAHs is a potentially important source of prebiotic compounds of the kind that could have lead to life on Earth.

It has been suggested previously that the major prebiotic building blocks for life originated from external sources, mostly being delivered to Earth on interplanetary dust particles (IDPs). G. Flynn et al. (Plattsburgh State Univ. of New York) reported results from a spectral study of IDPs which combined high resolution Fourier Transform Infrared (FTIR) Spectroscopy with Scanning Transmission X-Ray Microscope (STXM) observations on ultramicrotomed samples. The techniques discussed can detect and resolve weak C-H features in IDPs not observable by conventional laboratory methods. Combining these two techniques enabled determination of both the bulk and relative abundances of carbon-bearing species in samples, as well as their spatial distribution within samples. Results indicated that IDPs contain significant abundances of long-chained aliphatic hydrocarbons, suggesting that IDPs could have contributed important prebiotic compounds to the early Earth.

The announcement in August of 1996 of possible evidence for fossil life in martian meteorite, ALH84001 (D. McKay et al. 1996 *Science*), has intensified NASA's interest in exploring for ancient life during the upcoming Mars Global Surveyor Program. In this talk, McKay (NASA JSC) et al. provided an update of recent progress in assessing their biological hypothesis for ALH84001. Additional observations since the '96 report strengthen the case for 1) light carbon isotopic values in the

carbonate globules that contain the putative biosignatures (–55 to –65 ‰), interpreted to be due to biological fractionation, 2) biofilm-like textures in the carbonates, 3) chains of magnetite grains similar to those produced by terrestrial magnetotactic bacteria, and 4) oxygen isotope values indicative of low temperatures. Although it was noted that individually each of these lines of evidence can be explained by abiogenic processes, taken together, they provide a compelling argument for the presence of life. Recent work by other authors has challenged the biogenicity of features identified by McKay et al. as indicative of past life. However, based on a systematic review of recent work, McKay et al. concluded that the case for their original biological interpretations for the meteorite and for the existence of early life on Mars as been strengthened.

J. Kerridge (UC San Diego) provided a counter-argument to the proposal from D. McKay et al. that ALH84001 contains evidence of ancient biogenic activity on Mars. Kerridge noted that every line of evidence presented by McKay to support the biological hypothesis can also be explained by inorganic processes. And although multiple lines of evidence are certainly desirable, in his judgment, the evidence presented in favor of a biogenic origin fails to meet the stringent criteria required for a convincing case. Because of the uncertainties intrinsic to analysis of trace organics and potential contamination from long exposures to the Antarctic environment, Kerridge also argued that further investigations of martian meteorites are unlikely to provide more satisfactory evidence. Robotic missions to Mars are therefore essential, in which selected samples of sedimentary rocks are returned to the Earth for analysis. A realistic estimate of the first such sample return missions is 2008.

C. Chyba (Univ. Arizona) presented an analysis of possible liquid oceans beneath the ice sheet of the Galilean satellite, Europa. He noted that the presence of liquid water elsewhere in the solar system would be highly significant as a model of the early Earth at the time of life's origin. Chyba described a potential future European mission to test the hypothesis of an ocean, focusing on the ability of radar to provide evidence of liquid water. There are several unknown factors related to the transparency of ice to radar and how to best select a wavelength most likely to penetrate several kilometers of ice. Given the assumptions required by our present knowledge, it is possible to set a constraint of 10 km as the maximum ice depth beneath which water could be detected using radar.

S. Mojzsis and G. Arrhenius (Scripps Inst. Oceanography) and colleagues, described recent results that significantly push back the oldest record of biogenic activity on the Earth. In this research, high grade metamorphic rocks of the Isua region of southern Greenland were investigated using stable isotope analysis. It is generally considered that the Isua rocks are of early Archean age (3.6 - 3.9 Ga) and contain the oldest evidence of marine sedimentary systems. The high grade meta-sedimentary rocks studied include phosphatic mineral grains (apatite) containing graphite inclusions. Carbon isotopic analysis of the inclusions showed the graphite was isotopically lighter (by as much as –37‰) than matrix graphite included in whole rock analyses of the same rocks. On Earth, the precipitation of phosphate in sediments is thought to be biomediated and organic materials and organisms are often incorporated into the mineral grains that form. The observed isotopic difference in the phosphate hosted carbon and the matrix carbon was explained by the stability of phosphate during metamorphism. Thus, the isotopic values of the phosphate carbon are interpreted to be closer to primary, The depleted nature of the carbon isotope signatures is consistent with biological fractionation. This implies that life was present at 3.9 Ga and that the prebiotic processes leading to the origin of life on the Earth predate this estimate. These results support the case that the search for phosphate mineral deposits on Mars is an important aspect of the strategy to explore for a martian fossil record.

G. Joyce (Scripps Research Inst.) discussed a catalytic system which permits continuous evolution of a population of RNA molecules. This system is characterized by a cyclic process in which DNA is synthesized from an RNA template, and then RNA from the DNA in a second catalyzed polymerization reaction. The system can be made to evolve by introducing errors into the resulting RNA polymers followed by selective amplification of RNA molecules having a desired catalytic capability. In past work, this cycle was carried out in batches, with ten or more batch steps required to produce changes in the

RNA function. More recently it was found possible to carry out the process in a continuous mode by introducing a ligation reaction that allows newly synthesized RNAs to catalyze a reaction immediately. In one example of continuous evolution, RNA with catalytic abilities were amplified by a factor of 10298, with new rounds of synthesis occurring every five minutes. Joyce reported the evolutionary synthesis of a DNA enzyme that promotes a reaction analogous to the peptidyl transferase activity of bacteria in which peptides such as gramicidin are synthesized.

SESSION III

D. Lies and Y. Pendleton, Co-Chairs

J. Dickens and W. Irvine (Univ. Massachusetts, Amherst) are studying the molecular complexity and evolution of gas phase interstellar molecules in dense molecular clouds. Dickens provided an overview of the relation of the observed interstellar molecules to the chemistry of the primitive solar system objects we observe today. The identification of new species in both the interstellar and cometary environments provide additional links between the two regions. Important results include the first detailed mapping of HCN and HCO⁺ in cometary comae. The HNC/HCN abundance ratio is much higher than that predicted by equilibrium chemistry, and is similar to the values found in the interstellar medium, thus suggesting that some of the cometary HNC may be preserved interstellar matter.

L. Allamandola (NASA Ames) presented a brief review of the role of infrared spectroscopy in the identification of organic material and ices in the interstellar medium, and illustrated the connection between those materials and planetary systems which form from the dust and gas around young stars. The role of laboratory astrophysics in the identification of spectroscopic signatures observed from interstellar dust has proven to be essential in understanding the composition, evolution, and distribution of the basic building blocks which eventually led to life on Earth. This talk presented results on the photochemistry of interstellar ices, and emphasized the potential prebiotic role of some of these species. The formation of complex organics from simple starting mixtures in the laboratory suggests that comets may have delivered these materials to the early forming Earth such that they played a role in the evolution of life on this planet.

F. Freund (SETI Institute), with A. Gupta, discussed their work on the formation of complex oxygenated organic molecules from water and carbon dioxide within minerals and rocks. Water and carbon dioxide trapped in minerals breaks down to hydrogen gas, reduced carbon and peroxides, which then can combine to form carbon-carbon, carbon-hydrogen, and carbon-oxygen bonds. They showed that such processes can take place in artificially formed minerals in the lab and that the products of these processes can be found in naturally occurring olivine crystals, providing a potentially rich source of complex organic compounds for the evolution of early life.

A. Pohorille (NASA Ames), with M. Wilson, M. New, and C. Chipot, spoke about the ability of small synthetic peptides residing at interfaces between a nonpolar phase and water acting in functions reminiscent of rudimentary membrane transport and signaling functions. Starting from disordered structures, these peptides can organize into defined secondary structures, either in the nonpolar phase or along the interface, depending on their primary sequences. Some of these ordered structures can change orientation in response to electric fields and others, in pairs, can perform unidirectional proton transport.

D. Deamer (UC Santa Cruz) discussed using liposomes containing catalytic nucleic acid-replicating systems as mimics of early processes in the origin of cellular life. His group has been able to get lipids representing those found in meteorites, as well as natural lipid material extracted from meteorites, to form bilayer vesicles resembling membranes in many properties. By using lipids with appropriate chain lengths, vesicles can be formed that are permeable to mononucleotides but not oligonucleotides.

The inclusion of nucleic acid-replicating enzymes in such vesicles allows the synthesis of nucleic acids, which are retained inside the vesicles, from exogenously supplied mononucleotides.

B. Pierson (Univ. Puget Sound) spoke on the role of modern phototrophic microorganisms in the oxidation of iron in hot springs as a model for such processes in the early history of the Earth and with the goal of finding useful biogeochemical signatures due to this metabolism. Her group is examining the effects of the phototrophic microorganisms in one particular thermal iron spring on oxidized iron accumulation in the mats, and has been able to determine profiles for both oxygen concentration and pH levels, with changes that depend on day/night cycles. They are also looking for evidence for photoferrotrophy (direct photo-oxidation of iron by microorganisms) at this spring.

D. Ward (Montana State Univ.), with T. Papke, discussed studying cyanobacterial populations in modern hot spring mats as models for stromatolites, the major extant fossils of Precambrian microbial life. Morphology and culture alone are insufficient to define the populations in modern mats, so they have been using molecular techniques to examine the relatively slowly evolving ribosomal RNAs and more rapidly evolving rRNA intergenic spacers. They have seen distinguishable populations of genetically very similar cyanobacteria across thermal gradients and vertical spacial gradients in these mats, indicating that perhaps these may be different species inhabiting unique niches.

D. DesMarais (NASA Ames), with A. Tharpe and J. Thompson, discussed the use of $\delta^{13}\text{C}$ values to follow biogeochemical carbon cycling and its application to ancient deposits. In addition to primary production and bacterial degradation of carbon compounds, secondary production sustained by the oxidation of organic carbon or inorganic sulfur was also shown to be important in affecting $\delta^{13}\text{C}$ values in certain environments. Thermal alterations also affect these values, but affect the elemental H/C ratio as well. Thus plotting H/C vs. $\delta^{13}\text{C}$ can help determine the extent of thermal alterations. Using this approach, these investigators demonstrated that thermal alterations of mid-Proterozoic and Neoproterozoic kerogens were lower than previous estimates.

A. Knoll (Harvard Univ.) spoke on using the current wealth of information about the Proterozoic fossil record to predict general aspects of life prior to that period. For cyanobacteria, morphologic diversity is predictive of speciation and had already occurred to a major extent by the early Proterozoic. For eukaryotes, however, diversification occurred more during the Proterozoic and Mesoproterozoic periods.

B. Jakosky (Univ. Colorado, Boulder) discussed the biological potential of Mars based on the availability of energy necessary to drive living processes. Using the assumption that early life was primarily hydrothermally driven, he estimates that Mars, which has been calculated to have only about 1% of the volcanic activity of Earth, probably only developed life over the 4 billion years of its existence to a level comparable to 40 million years of Earth evolution. He also predicts a similar situation for Europa, since it has been calculated to have slightly less energy than Mars.

SESSION IV

L. Allamandola and B. Pierson, Co-Chairs

In the paper on *The NASA Specialized Center of Research and Training (NSCORT) in Exobiology*, J. Bada (UCSan Diego) et al. presented a global summary of the past 5 years of NSCORT activities in San Diego. The program started in 1992, with an annual budget of about \$1,000,000. The senior staff now consists of six PIs and an Outreach Coordinator. The bulk of the money is used to support young scientists in this new field of research. The main emphasis is on the origin of life. Activities span the range from prebiotic chemistry (including extraterrestrial materials); to chemistry in the pre-RNA world; as well as the early chemistry of the RNA world extending to the formation of DNA and simple proteins. Prior to the formation of the NSCORT program at San Diego, the PI's citation impact factor was 290.

Several years into the NSCORT program, this rose to 480, attesting to the efficacy of the collaborations and cross fertilization permitted under the auspices of the NSCORT program. The San Diego NSCORT group also organizes meetings and sponsors internship programs.

Interesting results on the positive detection of small (less than 10%) enantiometric excesses of certain amino acids in the Murchison and Murray meteorites were presented by J. Cronin (Arizona State Univ.) and S. Pizzarello in their paper entitled *Enantiometric Excesses in the Amino Acids of Carbonaceous Chondrites*. To minimize the possibility of confusion arising from contamination, the amino acids selected for study were those not occurring in the Earth's biosphere. An important conclusion of this work is that there exist extraterrestrial processes that can produce enantiometric excesses in amino acids which contain alpha methyl groups. Amino acids which lack alpha methyl groups were found to be racemic. The excesses seem to be consistent with production from irradiation processes by neutron stars. This theory is at a very young stage.

In *Modification of Amino Acids at Shock Pressures of 3.5 to 32 GPa*, S. Chang (NASA Ames) et al. investigated the effects of shocking amino acids under conditions which simulated the impacts between these meteorites during their residence in the asteroid belt and with the Earth's surface. A key question is to determine whether or not the compounds present in the meteorite could have been altered or destroyed by these collisions. Some of the results showed that most amino acids were destroyed in collisions with energies between 15 and 25 GPa. The small fraction of amino acids that survive this energy retain their optical activity. Secondary products are formed, however, which could have prebiotic significance. These include amino acids such as alanine, glycine, and γ - and β -aminoisobutyric acid. It was found that alpha-amino isobutyric acid is one of the more stable amino acids.

Over the years, the organic inventory of potentially important prebiotic molecules in meteorites has shown that many of these species are indeed present. Notably absent however are sugars, very important molecules in living systems due to their energy content. Their absence from the list arises in part because they are not as readily detected with the usual techniques. Simple sugars have been postulated to be formed extraterrestrially by reactions involving formaldehyde in a slightly basic solution. In the paper, *An Investigation of Sugars and Other Possible Formaldehyde Products in the Murchison Meteorite*, G. Cooper (SETI Institute) presented a targeted search for sugars, seeking to ascertain the importance of the formaldehyde reactions. A variety of simple sugars were found, supporting the importance of these reactions in the Murchison meteorite's history. Isotopic studies showed that these sugars (polyols) are indigenous to the meteorite and not due to contamination. However, the cyclic sugars - so important in today's metabolism - were not reported.

In *Co-Origin of Metabolism and Biopolymer Synthesis Using Formose Sugar Substrates*, A. Weber (SETI Institute) presented a new perspective on the prebiotic processes that could have been involved in the origin of metabolism and biopolymer synthesis. Considering the thermodynamics of a wide variety of prebiotic molecules, it was shown that sugars are the most reduced substrate possible for biosynthetic processes. This makes sugars a very attractive driver of many important reactions. For example, it was demonstrated that viewed from the thermodynamic perspective, redox disproportionation of sugar carbon accounted for about 90% of the total energy amino acid and lipid biosynthesis whereas ATP accounted for less than 10%. Thus, the author postulates that redox disproportionation of carbon, and not ATP, is the primary energy source driving important biosynthesis from glucose. An excellent case was made that since sugars are strong reducing agents, they can be almost viewed as "batteries," powering these important processes.

R. Blankenship (Arizona State Univ.) presented a talk co-authored with H. Hartman on *The Origin and Evolution of Oxygenic Photosynthesis* in which they presented a model for the origin of the contemporary oxygen-oxidizing tetranuclear Mn complex from an ancestral binuclear Mn catalase that may have used H_2O_2 as a reductant for a purple bacterial type of reaction center.

J.P. Gogarten (Univ. of Connecticut) presented a paper co-authored with E. Hilario and L. Olendzenski, *Horizontal Gene Transfer: Pitfalls and Promises* in which they presented ancient horizontal gene transfer events from Bacteria into Archaea as an explanation for many of the homologies occurring between metabolic genes from these two groups. The genes involved in the essential core activities of genome structure and expression and chemiosmotic coupling were less prone to horizontal transfer and therefore form the backbone of current phylogenies.

D. Lies presented a paper co-authored with A. Tsapin, J. Scott, and K. Neilson (*Genes and Enzymes of Anaerobic Metabolism in Shewanella putrefaciens*) in which they demonstrated techniques for isolating and characterizing the diverse electron carriers and reductases used by *Shewanella putrefaciens* which can grow on a wide range of electron acceptors. A soluble multi-heme c-type cytochrome with a range of redox potentials was detected as well as a high degree of homology among the diverse reductases making the sequencing of the whole genome of this extremely versatile organism a high priority.

E.I. Friedmann (Florida State Univ.) and several co-authors presented a paper (*Viable Bacteria in Siberian and Antarctic Permafrost*) in which they demonstrated viable bacteria in permafrost more than a million years old. These mesophilic bacteria (including anaerobes) decreased in number and diversity with depth but remained viable in the absence of growth.

C. McKay (NASA Ames) presented a paper co-authored with D.T. Anderson, W.L. Davis, and E.I. Friedman on "Polar Analogs to Mars" in which they proposed that if early Mars has been cold, this may have enhanced preservation of traces of life that existed in geothermally warmed permafrost.

SESSION V

S. Cady and C. Chyba, Co-Chairs

The *End Permian Mass Extinction Geochronology and Patterns of Extinction* was discussed by D.H. Erwin (Smithsonian Institute). The mass extinction event at the end of the Permian was the most extensive biotic crisis in the history of life. Determining its cause, however, has been hampered by a lack of high precision ages. Discriminating between possible extinction patterns and causes of the extinction requires high-resolution geochronological age determinations and precise stratigraphic information on taxon occurrences. Erwin and colleagues reported new uranium-lead-zircon data from Late Permian and Early Triassic rocks in South China (i.e., from volcanic ash beds interbedded within numerous Permo-Triassic (P-T) marine boundary layer sections) that provide the first constraints on the duration of the extinction. By demonstrating that the final pulse of extinction occurred in less than 1 million years, the author's findings provide insight with regard to the rates of paleontological and geochemical change that occurred during the close of the Permian, and provide critical data needed to test possible extinction scenarios.

A.I. Miller's (Univ. of Cincinnati) research addresses the extent to which the evolution, diversification, and extinction of advanced life in the Ordovician Period may have been mediated by physical processes and events. By compiling a database that depicts occurrences of the Ordovician genera in strata worldwide, and including data concerning the paleogeographic, paleoenvironmental, and geological settings of each occurrence, Miller can investigate, over scales ranging from local to global, whether the proliferation event at the end of the Ordovician Radiation was focused geographically or environmentally. In the paper entitled *Ordovician Biodiversity: Geography and Environment*, results to date were reported which include recognition that most of the global diversity increase was concentrated in the first half of the period, and that a geographic linkage exists between Ordovician radiation and likely regions of tectonic activity. Proximity to tectonic activity has been found to affect the diversification attributes differently for each paleocontinent. Although Ordovician genera expanded their geographic environmental ranges with age, preliminary results indicate that the Late

Ordovician mass extinction may have selectively eliminated taxa within limited geographic ranges, raising the possibility that this event was also selective with respect to taxon age.

Two possible causes of the apparent low-latitude glaciation in Earth history during the Huronian (~2.2 billion years) and again in Late Proterozoic (~ 750 - 550 million years) include either a shift in the Earth's obliquity ($> 54^\circ$) or the possibility that at those times the surface of the Earth was completely frozen over. A strong argument against the later hypothesis is that a global ice blanket would likely have eliminated all photosynthetic life on the planet, a phenomenon not supported by the fossil record. To reconcile the geological and fossil record, D.M. Williams (Penn State Univ.) and colleagues have developed a self-consistent model that can account for a rapid drop in obliquity during the last glacial period as a consequence of climate friction and changes in the Earth's oblateness. The title of their paper posed the pertinent question: *Was High Obliquity the Cause of Low-Latitude Precambrian Glaciation?* Although changes in the Earth's oblateness (hence obliquity) due to massive water displacement during glaciation are usually considered to be negligible, the authors have noted that these effects were likely to have been significant during the late Proterozoic when the bulk of the Earth's continents are thought to have been clustered around the South Pole. The authors calculate that a decrease in the early Earth's obliquity from 55° to 25° could have occurred in under 150 million years, and that such an event process would bring the Earth's obliquity close to its present value of $< 25^\circ$ by 430 million years.

In *Paleobiology Of The Terminal Proterozoic: Prelude To The Cambrian Explosion*, B. Runnegar (UCLA) et al. examine the geologically most obvious biological event in the history of the Earth, the Cambrian explosion of complex life. Much of the research aimed at understanding this milestone in the evolution of life has focused on evidence from well preserved fossils in the Cambrian such as the Burgess Shale. Although many of the evolutionary innovations were underway before the beginning of the Cambrian, the oldest metazoan trace fossils are no older than about 550 million years. Recent discoveries of Ediacaran trace fossils and associated carbonate skeletons in late Proterozoic rocks in Namibia and Nevada provide a glimpse of biodiversity at the close of the Proterozoic that cannot be traced in the Metazoa. Runnegar's research into the evolutionary innovations displayed by Ediacaran fossils at the terminal Proterozoic indicate that the synchronous appearance of distantly related clades of megascopic organisms point to the poverty of intrinsic rather than extrinsic explanations for the nature of the Cambrian explosion of multicellular life.

Y. Yung (Cal Tech) and co-workers reported on their studies of the effects of SO_2 on the middle atmosphere of early Mars in *CO₂ Greenhouse in the Early Martian Atmosphere: SO₂ Inhibits Condensation*. Ten years ago the ancient climate on Mars was considered to have consisted of a dense carbon dioxide atmosphere that would have kept the planet's surface temperatures above the melting point of water. Subsequent models that also considered the effects of CO_2 condensation, however, revealed that the presence of CO_2 by itself would have been inadequate to sustain liquid water on Mars. By incorporating small amounts of SO_2 in their preliminary one-dimensional radiative model of an early Mars atmosphere, Yung and co-workers have found that the middle atmosphere of early Mars may have been kept warm enough to inhibit the condensation of CO_2 . An intriguing consequence of their model is that the presence of a small amount of SO_2 in a martian atmosphere may also have provided an effective UV shield for a hypothetical martian biosphere.

A. Zent (NASA Ames) and R. Quinn presented results from their work modeling the diffusion of photochemically produced hydrogen peroxide in the martian atmosphere down into the martian regolith. This question is important for future searches for life or organic molecules on Mars: For organics to survive in the martian soil, they must lie beneath the depth to which oxidants such as hydrogen peroxide will diffuse. Quinn and Zent's work suggests that regolith mixing rather than diffusion may be the dominant mechanism of oxidant transport in the martian regolith, depending on destruction rates for hydrogen peroxide in martian soils.

T. Bunch (NASA Ames), D. Des Marais, L. Becker, W. Wolbach, J. Bada, and D. Glavin discussed the effects of the Sudbury impact event on organic matter. They note that the Sudbury Onaping formation impact deposits are exceptionally carbon rich. The goals of their investigations are to characterize the carbonaceous components and their distributions, identify their potential sources, model pressure-temperature-time conditions in the impact and establish when life reappeared in the region. Interestingly, they argue that the impact may actually have helped life to reestablish itself rapidly in the region, by furnishing nutrients and favorable environments.

K. Pope (Geo Eco Arc), K. Baines, and A. Ocampo examined meteorite impact production of volatiles and their biospheric effects at the Cretaceous/Tertiary (K/T) boundary. In order to assess global average environmental results of the K/T impact, they use estimates of volatiles in the projectile and target rocks at the Chicxulub site to predict the mass of carbon dioxide, sulfur dioxide, and water vapor globally distributed in the stratosphere by the impact. They conclude that global warming due to carbon dioxide generation was less than 1 degree centigrade, insignificant compared to cooling due to sulfates.

C. McKay (NASA Ames) and B. Borucki used numerical and experimental techniques to model the composition of an atmosphere dominated by cometary volatiles. They find that comet collisions on early Earth should yield carbon dioxide and methane about equally, but little carbon monoxide. Comet shocks do not produce ammonia, so that nitrogen will be in the form of molecular nitrogen rather than ammonia. These results have obvious implications for the chemical composition of the early terrestrial atmosphere, were that atmosphere in fact dominated by impacts.

Finally, T. Wdowiak (Univ. Alabama, Birmingham), D. Agresti, S. Mirov, and A. Kudryavtsev described their development of a laser Raman spectrometer for in situ exobiology exploration. They have demonstrated that the spectrometer may be calibrated using Fraunhofer lines of the solar spectrum obtained from atmospherically scattered sunlight, and that their laser signal will transmit through an optical fiber cooled to as low as -132 degrees centigrade. Both these demonstrations are important for the use of such an instrument on Mars. The group continues to obtain laser Raman spectral signatures of particular interest to planetary exploration and exobiology.

SESSION VI

T. Kanavarioti and D. Lowe, Co-Chairs

The presentations in Session VI focused on models for prebiotic self-replicating systems based on nucleotides or nucleotide analogs, on simulation experiments to mimic Titan's atmospheric chemistry and hydrothermal vent conditions, and on the identification of biomarkers associated with hydrothermal vents, spring systems and lake formations.

C. Switzer (UC Riverside) opened the session by reporting on the ability of 2'-5'-linked RNAs to act as templates and successfully direct the synthesis of a mixture of natural and non-natural oligonucleotides. Work on non-natural nucleobases, such as iso-cytosine and iso-guanine, which could potentially be used in place of the natural nucleobases was also presented.

L. Orgel (Salk Institute), with co-author M. Koppitz, discussed experiments which showed that peptide nucleic acids, PNA, can act as templates for RNA synthesis and vice versa. In addition, the chemistry was explored so that a PNA or DNA template can successfully direct the ligation between a DNA and a PNA (chimera).

J. Ferris (Rensselaer Polytechnic Inst.) and co-author D. Clarke, described experiments which simulate Titan's atmosphere and will be instrumental in helping explain the data returned from the Huygens probe of the Cassini mission. Photolysis experiments with acetylene and cyanoacetylene

resulting in polymerization and characterization of the products was done with scanning electron microscopy (SEM) as well as with chemical methods.

B. Simoneit (Oregon State Univ.) and co-authors T.M. McCollm and G. Ritter described laboratory experiments that simulate the tentative chemistry involved in prebiotic hydrothermal systems. Formic acid and oxalic acid were exploited as the carbon source and during Fisher-Tropsch-type synthesis yielded a number of organic compounds ranging from C 2 to C 35.

Research from E.L Shock's group (Washington Univ.) argues in favor of the existence of hydrothermal vents in a planetary context and addresses the possibility that they existed in Europa and that they might have fostered life.

In *Anoxia and Evolutionary Patterns in the Deep Sea: On-Shore/Off-Shore Trends and Recent Recruitment of the Deep-Sea and Hydrothermal Vent Faunas*, D.K. Jacobs (UCLA) and D.R. Lindberg emphasized the importance of anoxic events in the deep oceans in regulating biological evolution. They note that the observed tendency for higher biological taxa to originate onshore and diversify offshore is not uniform over time. Onshore origination of higher taxa is more characteristic of intervals when there is strong deep-water anoxia, such as the middle to late Mesozoic, but an offshore origin is favored in the Cenozoic, when the deep oceans have been more highly oxygenated. Periodic deep-ocean anoxia should also affect deep-water hydrothermal vent organisms, which are either oxygen users or require redox gradients to survive.

T. Wdowiak (Univ. Alabama, Birmingham) and colleagues reported on a study in which a Mössbauer spectrometer was used to identify nanophase iron-bearing materials in hot springs in Yellowstone National Park and Colorado. In *Mössbauer Signatures that may be Useful in Identifying Residues of Ancient Martian Hydrothermal Systems*, nanophases detected included siderite and nontronite. Both should be easily detectable in martian materials using Mössbauer techniques and could serve as keys to identifying martian hot spring deposits.

In *Exploration of Mono Lake Using TROV: Application of Telepresence Technology to Exobiology Studies*, C.R. Stoker (NASA Ames) reported on use of the TROV (Telepresence-Controlled Remotely Operated Vehicle) in Mono Lake to examine tufa towers and the chemistry of the subsurface springs that formed them. A number of sites were visited, including some tower-like features that were not tufa towers.

S.L. Cady (SETI Institute) and colleagues reported on a study aimed at recognizing hyperthermophilic biogenic signatures that might be preserved in the rock record on either the Earth or Mars. The studies reported on in *Recognizing Biogenic Signatures Near Life's Upper Temperature Limit: The Role of Hyperthermophilic Biofilms in Spicular Geyselite Morphogenesis*, demonstrate that the morphology and deposition of spicular geyselite in the high temperature parts of hot springs are controlled by hyperthermophilic biofilms and that different biofilm communities exist in subaerial and subaqueous parts of the hot spring system.

Early organisms may have not only lived in and around hydrothermal springs but also evolved there. In *Fossilization Processes in Thermal Springs: Comparative Studies of Modern and Ancient Siliceous Spring Systems*, J. Farmer (NASA Ames), B. Bebout, L. Jahnke, D. Des Marais, and M. Walter, studies of modern hot springs systems show that microbial signatures are preserved in a number of ways, including cellular fossils, biofabrics, and biosedimentary structures. In both modern and ancient deposits studied, organically preserved microfossils are rare: most organic matter is quickly removed by oxidation. More common are silica coatings on organic grains and morphological structures formed by biological activities.

SESSION VII

P. Knauth and A.L. Weber, Co-Chairs

D. Lowe (Stanford Univ.) described the Ikiryu sinter, a siliceous hot-spring deposit near Kuju Volcano, Japan. The deposit includes: (1) a lower member composed of dense, recrystallized largely structureless chert and (2) an upper member consisting of white siliceous sinter showing well preserved layers of conical stromatolites, and silicified filaments, streamers and sheet-like mats.

J. Fredrickson (Pacific NW National Lab.) reported on the preservation of haloarchaea and their 16S rDNA in brine inclusions from bedded salt deposits. Viable haloarchaea and their 16S rDNA were found in four-year-old (modern) Laguna Grande de la Sal salt, but not 200 m.y. polyhalite from the Salado Formation in New Mexico.

R. Mancinelli (SETI Institute) presented data on the survivability of osmophilic microbes exposed to the space environment for two weeks aboard BIOPAN (a biological facility developed to fly in Earth orbit on recoverable satellites). The osmophilic microbes survived the two week exposure. The major cause of cell death was DNA damage which was greater in vacuum-UV exposed cells compared to vacuum-only exposed cells.

G. Fox (Univ. Houston) described his studies of the origin of the translation machinery that involved testing the ability of aminoacylated-tRNA molecules to form peptides in the absence of ribosomes. He reported that aminoacylated-tRNAs yielded dipeptides in the absence of both synthetase and ribosomes when Ala-His was used as a catalyst/cofactor.

K. Zahnle (NASA Ames) presented a case against the cometary origin of the oceans. He argued that late-accreting volatile-rich veneers (either asteroids or comets) appear to be quantitatively inadequate. He proposed that the water of the inner solar system could have come from objects falling from an augmented ancient asteroid belt, or scattered planetesimals associated with the accretion of Jupiter.

Y. Pendleton (NASA Ames) reviewed studies of organic solid-state materials in space that show remarkably similar absorption features (attributed to aliphatic hydrocarbons) amongst interstellar dust clouds in our galaxy, dust-embedded distant galaxies, and the Murchison meteorite. Comparison of these infrared observations with laboratory processed organic residues suggests that energetic processing of simple ices results in materials similar to those seen in space.

S. Charnley (UC Berkeley) showed that the observed gas phase interstellar D/H ratios in CH₂DOH and CH₃OD are lower than expected solely from formation on grains, and that chemical reactions must also be forming CH₃OD in the gas phase. He also extended the general surface reaction scheme (based on organic radical stability) to oxygen and nitrogen atom additions to carbon chain radicals.

S. Benner (Univ. Florida) speculated on the identification of structures of modern terrestrial biochemistry that are unique solutions to challenges faced by living systems in general. Since these structures would be required for life, they would also be found in extraterrestrial life. His analysis indicated that nucleic acids show some structural features that are likely to be universal, and others that are not.

R. Krishnamurthy (UC San Diego) described the mineral induced phosphorylation of glycolaldehyde to give glycolaldehyde phosphate. Glycolaldehyde phosphate and glyceraldehyde-2-phosphate have been shown to condense under prebiotic conditions to give ribose-2,4-diphosphate which is considered a precursor of primitive p-RNA (an RNA analog containing the pyranose form of ribose and 2' → 4' linkages).

D. DeVincenzi (NASA Ames) reviewed the requirements for Planetary Protection that might be imposed on a Mars Sample Return Mission. In light of the recommendation of the Space Studies Board that the samples returned from Mars should be contained and treated as though potentially hazardous until proven otherwise, he discussed the need to: (1) assure sample containment, (2) quarantine and detect possible biological entities and/or organics in the sample, and (3) determine if the Mars samples are hazardous.

M. Race (SETI Institute) reviewed the legal and public concerns about the environmental impact and potentially hazardous nature of samples returned from Mars. She stressed that planetary protection must be integrated early into all phases of the sample-return mission design and that NASA must keep other government agencies and the public informed of the decision making and review process. Areas that have recently received special attention are: (1) consideration of the environmental impact statement, (2) identification of legal ambiguities and scientific uncertainties, (3) development of a systematic biohazard testing protocol for returned martian samples, and (4) studying public risk perceptions and responses.

SESSION VIII

L. Jahnke and T. Wdowiak, Co-Chairs

J. Hayes (Woods Hole Oceanographic Inst.), with colleagues H. Strauss and A.J. Kaufman, described their examination of the global biogeochemical cycle of carbon as inferred by ^{13}C abundances. Except for declines between 550 and 520 Ma, and about 29 Ma ago, the fraction of ^{13}C can be accounted for by the maximum set by the physiology and enzymology of marine algae. The observed declines can be attributed to increased rates of planktonic growth and a decreased abundance of CO_2 .

L. Jahnke (NASA Ames), R.E. Summons, and H.P. Klein have studied mid-chain, methyl-branched alkanes as a group-specific biomarker for cyanobacteria for the purpose of providing data of use in interpreting the ancient carbon record. They find that dimethyl alkane synthesis is linked to environmental factors in the case of contemporary thermal springs. This points to the utility of pure culture studies in interpretation of the fossil record.

Returning to ^{13}C , D. Kass (Cal Tech) and Y. Yung argue that on Mars carbon does not cycle through the environment as for Earth. It remains in the atmosphere-cap-regolith reservoir until lost from the planet by exospheric processes or conversion to carbonate. Unlike Earth, the carbonate is not subducted, making it a permanent sink. This difference argues against applying the terrestrial $\delta^{13}\text{C}$ isotopic system to Mars. Unlike Earth, the $\delta^{13}\text{C}$ of the atmospheric reservoir can change with time. They have initiated models and find the martian atmosphere "started out quite light and has progressively gotten heavier."

Using the 70 m Deep Space Network antenna at Goldstone, California, T. Velusamy (JPL), W. Langer, and S. Levin probed protostellar cores for long chain hydrocarbon molecules: cumulene carbenes ($\text{H}_2\text{C}=\text{C}=\text{C}=\text{C}$), acetylenes, and linear carbon chain radicals. The data allow tracking down the gas phase chemical pathways by which these species are formed as star formation proceeds.

M. Fomenkova (UC San Diego) and S. Chang have been mining the mass spectroscopy data base obtained during the Comet Halley fly-bys of more than a decade ago. They have been able to go beyond elemental abundances and have established the outlines of the molecular groups for the carbonaceous grain component of Comet Halley. Included are polymers of formaldehyde, HCN, and unsaturated nitriles. The nitrogen abundance in mixed grains (inorganic plus organic) is enhanced. This work provides a beginning bridge between interstellar matter and what is cometary/solar system.

D. Blake (NASA Ames), P. Jenniskens, and L. Delzeit tenaciously continue their dissection of the solid forms of the most exobiologically relevant molecule (you may recall their cover photo for *Science*). These researchers have mastered the transferable cold finger technique to track down all the varieties of transitions that can occur after water molecules alight on a cold interstellar surface (grain). The objective: to correlate things such as a comet outburst with structure defined by electron diffraction, etc.

The research of D. Usher (Cornell Univ.) focuses on the mechanism of the *de novo* formation of RNA in prebiotic times. This reaction is known to be catalyzed by amines, particularly alkanediamines, yet the mechanism of this catalysis has been a subject of controversy in recent years. The reported recent results show that the mechanism of amine-catalyzed cleavage of RNA appears to be simple general-base catalysis, however earlier work suggested that the actual mechanism of amine-catalyzed hydroxyl attack on a phosphate diester involves the kinetically equivalent protonated amine plus the deprotonated hydroxyl group. Their search continues for amine catalysts that can improve the yield of RNA oligomers in the *de novo* formation of RNA from nucleoside 2',3'-cyclic phosphates under simulated prebiotic conditions.

The ion exchange and catalytic properties of layered double hydroxides, along with solid state photo-reduction of carbonate through a ferrous iron presence commanded the attention of P. Braterman (Univ. of North Texas), K. Shannon, and J. Boclair. They find that conversion of carbonate to formaldehyde is not significant when 10 atom % iron(II) containing layered double hydroxides with carbonate are subjected to UV radiation. Iron(II) carbonate converts to a green rust of iron(II), iron(III) hydroxide carbonate. The layered double hydroxides do absorb the possible prebiotic ferrocyanide, and investigation of the reaction of ammonium magnesium ferrocyanide and formaldehyde shows evidence for a wide range of products, which are the study's next target.

For a long time to come, most of what we are going to learn about Mars will be through remote sensing from orbit. After all, the martian surface to be roved/walked upon is equivalent to the dry surface of Earth, and that took a little time to explore on foot. J. Orenberg (San Francisco State Univ.), A. Banin, T. Roush, and S. White continue their effort to produce laboratory analogs of martian soil and characterize them with reflectance spectroscopy and other physical methods, including x-ray diffraction. The precursor material for the analogs is partly palagonized volcanic tephra. The analogs are "weathered" with acids (H_2SO_4 , HNO_3 , and HCl). In the visible and near IR (250-2500 nm), an increase in overall reflectance is noted and attributed to sulfate and salt mixtures. For the 2.5-25 micron IR region, the carbonate and sulfate bands are distinct; however, neither nitrate nor phosphate can be detected.

L.P. Knauth. (Arizona State Univ.) reported on his studies of the early evolution of life in non-marine environments. Some non-marine deposits contain microfossils, as until oceanic salinity decreased to acceptable levels, early evolution of life may have been especially active in the lower salinity, non-marine waters in lakes, rivers, and soils. Microfossils of probable cyanobacteria have been found in the associated secondary silica in paleokarsts as old as 1200 m.y. Knauth et al. seek to identify silica and carbonate that formed in early subaerial and other non-marine environments and explore further the newly emerging fossil record of life on land in the Precambrian. The preservation of organisms in this type of silica is currently being examined and ancient examples are a new target material for exploring the fossil record of life on land in the Precambrian and possibly on Mars. Calcite alteration veins in terrestrial basalts are being similarly examined and may provide easily accessible target material for future sample returns from Mars.

SESSION IX

T. Bunch and J. Orenberg, Co-Chairs

The session began with a presentation by H. Levison (Southwest Research Institute) and J. Lissauer entitled *The Diversity of the Outer Planetary System*. The authors created a set of plausible outer planetary systems using direct numerical integrations. Included in these simulations were the effects of the solar nebula. This included the accretion of nebular gas in order to form Jupiter-like planets. It was found that some sort of dissipation was required for time scales longer than 10 million years in order to construct systems like ours. The number of planets can vary from one to seven. Systems with a large number of planets never contain large, Jupiter-like planets, but instead are made up of Uranus-like planets. Stable planetary systems can include planets in mean motion resonances with one another. Perhaps most surprisingly, it is possible to construct stable systems in which the planetary orbits can undergo large, semi-periodic changes.

G. Wetherill (Carnegie Institution of Washington), S. Kortenkamp, and J. Chambers in a presentation entitled *Formation of the Asteroid Belt* emphasized the importance of asteroids in meteorite formation and their effect upon the earliest evolution of life on Earth. They presented a model of the formation of bodies interior to giant planets which suggests an asteroid belt population of 25 bodies as large as or more between Earth and Jupiter within a few million years. These bodies are removed from the asteroid region in about 100 million years due to collisions with each other. It was concluded that gas giants postdate the formation of Mars sized asteroidal bodies and asteroids interior to the gas giants because these giants would preclude the formation of such bodies.

In a presentation by P. Wannier (JPL) and co-authors P. Schloerb and G. Moriarty-Schieven entitled *The Route from Interstellar to Protostellar Abundances: Evidence of Variability in the Interstellar Medium*, the assumption that there is a steady evolution of nuclear abundances in the Galaxy resulting in a balanced enrichment of the elements considered essential for the evolution of life was tested. Observations were made on the scale of a solar mass, in this case on Rho Oph, a nearby, molecular cloud complex using the isotope pair O^{17}/O^{18} , the most precisely determined extra-solar abundance ratio. The group concluded tentatively that there are measurable variations in abundances on solar mass scales. The study will be extended to an examination of the nearest known interstellar molecular cloud, L1457, to allow confirmation of the tentative conclusion.

Spectroscopic Studies of Pre-Biotic Carbon Chemistry was the subject of a presentation by G. Blake (Cal Tech). His group is attempting to constrain the overall chemical budget of the biogenic elements during star formation processes. These studies are done using observational spectroscopy combined with laboratory and theoretical components. Imaging with Millimeter Arrays is designed to probe the critical coupling of phase and grain mantle in the prebiotic evolution of protoplanetary nebulae. Such molecules as HCN, HC_3N , CH_3CN , HNCO, CS, SO, SO_2 , OCS, HDO, CO, H_2CO , CH_3OH , and HCOOH were detected in comet Hale-Bopp at spatial resolutions akin to optical astronomy. In the lab, the extraordinarily complex prebiotic chemistry of carbon as reflected in interstellar and primitive solar system materials is being studied as vinyl radical, benzyne diradical and carbenes.

D. Woon (Molecular Research Institute) spoke about *Theoretical Studies of the Extraterrestrial Chemistry of Biogenic Elements and Compounds* as shown in gas-grain reactions which are thought to form molecular species (e.g., alcohols, ketones, aldehydes, and carboxylic acids) in interstellar and circumstellar clouds. The hydrogenation of CO to form the formyl radical HCO is important as a precursor to the formation of larger organic species. The hydrogenation reaction is greatly enhanced by icy surfaces comprised of water or other species. Theoretical *ab initio* calculations were conducted to elucidate the modifying effect of water on the hydrogenation reaction. The conclusion was that water has little impact on the energetics of the reaction, but does alter the potential energy surface of the reaction.

N. Lerner (NASA Ames) and D. Summers discussed their research concerning *Reduced Nitrogen on the Early Earth*. They suggested that one source of reduced nitrogen could be the fixation of nitrogen to NO by shock heating, followed by photochemical conversion of the NO into nitrite. Utilizing the ammonia by this reaction and non-reducing conditions could produce amino acids via the Strecker synthesis. Additional studies show that the Strecker synthesis does not appear to be hampered by the presence of iron. Thus the Strecker synthesis and the iron reduction of nitrite to ammonia can be combined to form amino acids from nitrite, ferrous iron, cyanide and formaldehyde.

A. Kanavarioti (UC Santa Cruz) reported on the *Preference for internucleotide Linkages as a Function of the number of constituents in a mixture*. Phosphoimidazolide activated ribomononucleotides are useful substrates for non-enzymatic synthesis of oligonucleotides. Product distributions were obtained in reactions with one, two or three reactive components at the same total nucleotide concentration. The most remarkable result of the experiments is that the nearly 2 fold increase of the percent yield of internucleotide-linked dimers is not due to a concentration effect, but to the increased complexity of the system. These observations may provide an example of how increased complexity in relatively simple chemical systems leads to organization of the material and consequently to chemical evolution.

M. Schoonen (SUNY, Stony Brook) and J. Bebie presented results on the *Interactions of Carbon and Phosphate with Pyrite in Aqueous Solutions*. Pyrite plays a central role in the chemo-lithotrophic model championed by Wächtershäuser where the redox couple is assumed to have reduced CO₂ or CO to simple organic compounds. Thermodynamic calculations for a temperature range of 0 to 300° C were made to evaluate the energetics of CO₂ reduction. Results show that the FeS-H₂S/FeS₂ couple drops with increasing temperature and the first step reduction of CO₂ to HCOOH is energetically unfavorable. In addition, FOT analysis indicates an energy barrier that prevents facile CO₂ reduction. Tests were also made to determine the effectiveness of pyrite as a scavenger of C-compounds and phosphates. Little interaction was shown by acetate, alanine, and glycine whereas phosphates were strongly retained on pyrite.

S. Awramik (UC Santa Barbara) and P. Buchheim discussed *The Meentheena Carbonate, Ancient Lakes, Facies and Exobiology*. The Carbonate Member has abundant and diverse stromatolites and rare microfossils that represents an important unit with significant exobiological implications for understanding ancient life in lakes. The Meentheena and its stromatolites indicate that during the late Archean microbial life thrived in lakes and, that despite higher atmospheric pCO₂ levels, carbonates preserving aspects of this fossil record can be widespread. The authors suggest that the search for evidence of ancient life on Mars, include lacustrine deposits with repeated sequences that might represent fluctuating water depths.

H.P. Klein (SETI Institute) presented *Mars Studies* about work that began as an outgrowth of participation on the Russian '96 mission, and was initially directed toward two aspects of that mission: involvement in the Mars Oxidant experiment (MOx), which was chosen to be flown on the small lander, and involvement in establishing geological criteria of exobiology relevance. Since the loss of that mission, Klein has continued work with other collaborators and extended the research to include characterization of the Ma'Adim Vallis-Gusev Crater region and the Ares Vallis region (the landing site for the Pathfinder spacecraft). Finding additional sites for exobiological study on Mars will be aided by continued analysis of Viking orbiter data. While ships sailing the interplanetary sea do at times make a safe transit (the Vikings, Pathfinder), some (Mars Observer, Mars '96) do not; Klein has experienced both situations. Given the 20-year plus gap between the Vikings and Pathfinder, it's good to have someone grounded on both sides.

ABSTRACTS of ORAL PRESENTATIONS

The abstracts for the oral presentations appear in order of presentation. The page number for any individual abstract can be found by the speaker's name in the *Speaker's Index* at the back of this document. The abstracts for the poster presentations are after those of the oral presentations and are in alphabetical order by the first author's name.

INFRARED CAVITY RINGDOWN LASER ABSORPTION SPECTROSCOPY OF CARBON CLUSTERS

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Pure carbon clusters are a virtually unexplored form of carbon that may be important in interstellar chemistry and the nucleation of solid matter. To advance astrophysical study of these species is the aim of this research.

We have previously studied carbon clusters as large as C₁₃ by infrared diode laser absorption spectroscopy¹, characterizing their structures, bonding, and properties. These data, supplemented by precise measurement of far infrared (10-200 cm⁻¹) bending frequencies permit the design of astronomical searches using Far-IR receivers aboard the KAO (or SOFIA) as recently demonstrated by the detection of C₃ in SgrB².

Here we describe a new approach for measuring infrared spectra of carbon clusters using cavity ringdown detection³. This method permits the measurement of very small absorptions (~1 x 10⁻⁶ fractional absorption per pass) with Doppler-limited precision, and with complete coverage of the mid-infrared. New results for carbon clusters will be presented.

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HYDROGENATED PAH (AN AROMATIC & ALIPHATIC SPECIES) AS A COMPONENT OF THE INTERSTELLAR AND CIRCUMSTELLAR MEDIUMS

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While the multi-ring molecules called polycyclic aromatic hydrocarbons (PAH) are of demonstrated astrophysical interest, is there relevance for exobiology? Very recent developments reveal the story of multi-ring structures in the interstellar and circumstellar mediums to be a richer one than previously imagined. Since its inception, the PAH hypothesis has been focused on large aromatic carbon structures having a minimum of hydrogen atoms at the periphery. The concept was driven by consideration of the necessary properties to explain the observed unidentified infrared (UIR) emission bands.

What is new is the idea that a fraction of the multi-ring structure need not be aromatic! Indeed, the aromatic portion may reside in the form of islands, which among other things could give rise to the 2175 Å interstellar extinction "bump." Other interesting aspects of hydrogenated PAH (or H_n-PAH) are the correlations of laboratory infrared spectra with 3 micron region emission from Orion and the proto-planetary nebula IRAS 05341+0852. It was this finding that initiated consideration of a molecular species that might be described as a "hybrid of" or "link between" aromatic and aliphatic molecular species. We have found additional evidence that the strength of the observed 6.2 micron (1600 cm⁻¹) UIR band, relative to others, may be a signature of an extensive hydrogenated PAH component of the interstellar medium. Also, the interstellar absorption known as the "diamond" band, through previous attribution to tertiary carbons at the surface of nanophase diamonds, can also be explained by hydrogenated PAH structures having molecular weights >1000 amu.

From the viewpoint of exobiology, the attractive aspect of hydrogenated PAH, as a cosmic species, is that the aliphatic fraction of these kinds of structures is a much more likely feedstock for processing into species that, on the basis of the terrestrial model, are considered to be prebiotics. The extensive aliphatic/cycloalkane fraction of large hydrogenated PAH structures can undergo cracking into smaller linear forms or be polymerized into kerogen-like material such as that found in carbonaceous chondrites. Hydrogenated PAH (H_n-PAH) can serve as an alternative (as compared to previous models) reservoir of the kind of material that can be processed into prebiotics.

IDENTIFICATION OF ORGANIC CARBON IN INTERPLANETARY DUST

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Modeling by Anders /1/ indicates interplanetary dust particles (IDPs) provided a significant amount of prebiotic organic matter to the surface of the early Earth. IDPs, ~10 microns in size, collected by NASA from the Earth's stratosphere, have an average carbon content of ~12% /2/. However, our Electron Energy Loss and Carbon-XANES measurements indicate that graphite is common in IDPs, and the ratio of organic to graphitic carbon has not been established.

Organic carbon in the form of polycyclic aromatic hydrocarbons (PAHs) has been detected in IDPs by Clemett et al. /3/ and Swan et al. /4/ have reported the Fourier Transform Infrared Spectroscopy (FTIR) detection of a "poorly resolved band around 2860 cm⁻¹" accompanied by bands at 2926 cm⁻¹ and 2960 cm⁻¹, a region characteristic of C-H stretching vibrations, in several IDPs. To follow-up on their report, we examined four IDPs using a Spectra-Tech u-FTIR installed on an infrared beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. This instrument has a signal to noise ratio ~100 times better than conventional laboratory FTIR instruments /5/, providing the sensitivity needed to detect and resolve the weak C-H features in IDPs.

Fragments, several microns thick, of three IDPs (L2008F13, L2008F16, and L2008G9) exhibited three relatively strong absorptions, at 2960 cm⁻¹, 2926 cm⁻¹, and 2854 cm⁻¹, and the best spectrum of L2008G9 also showed a weaker feature near 2870 cm⁻¹. The pair of features at 2926 cm⁻¹ and 2854 cm⁻¹ are characteristic of the C-H₂ symmetrical and asymmetrical stretching vibrations in an aliphatic hydrocarbon, while the pair of features at 2960 cm⁻¹ and 2870 cm⁻¹ are characteristic of the C-H₃ symmetrical and asymmetrical stretching vibrations.

An ultramicrotome thin-section, less than 200 nm thick, of the fourth IDP (L2009*F2), previously examined using the Scanning Transmission X-Ray Microscope (STXM) at the NSLS, showed absorptions near 2920 cm⁻¹ and 2850 cm⁻¹, the two strongest absorptions detected in the thicker IDP samples, consistent with the C-H₂ features. This demonstrated that STXM and u-FTIR measurements can be performed on the same IDP section, using the STXM to determine the bulk carbon abundance, the spatial distribution of the carbon, and the abundance of graphitic carbon, and using the u-FTIR to determine the types and relative abundances of the organic species present in the section.

These results indicate that IDPs contain significant abundances of long chained aliphatic hydrocarbons. Thus, IDPs could be an important resource for the development of life on Earth, other planets such as Mars, and moons.

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ADDITIONAL EVIDENCE FOR POSSIBLE BIOGENIC ACTIVITY IN THE MARTIAN METEORITE ALH84001

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Martian meteorite ALH84001 has been shown to contain evidence of possible past biogenic activity inside small carbonate aggregates or globules within the meteorite. The four lines of evidence presented by McKay et al. /1/ included the following: a) iron oxides and sulfides having textures similar to terrestrial biominerals, b) carbonates formed at temperatures capable of supporting biogenic activity, c) indigenous organic compounds in the form of PAHs associated with regions containing carbonate globules, and d) morphologies of segmented, spherical and elongated features similar to terrestrial micro-fossils and nanobacteria. None of these observations is in itself conclusive for the existence of past life. Although there are alternative explanations for each of these phenomena taken individually, when they are considered collectively, particularly in view of their close spatial association, it was concluded /1/ that they were evidence for primitive life on early Mars.

Since the report of McKay et al. /1/ additional observations have been collected which support a biologic origin for the globules including: i) carbon isotopic compositions (-55 to -65 ‰), ii) biofilm-like textures, iii) chains of magnetite grains within carbonate globules similar to those produced by magnetotactic bacteria, and iv) oxygen isotopic compositions within individual globules that are indicative of low-temperature processes /2/.

Alternative hypotheses for the origins of the globules have been directed toward the nature of the carbonate formation temperatures, magnetite morphologies and structures within the carbonates, the sizes of nanostructures within carbonate rims, and potential terrestrial organic contaminants (i.e. PAHs) introduced to the meteorite in Antarctica. The evidence, both pro and con, will be evaluated in light of recent research efforts that have been conducted since the initial proposal regarding potential biogenic activity in the martian meteorite ALH84001. After careful evaluation of the past and recent information on ALH84001, we feel that our 1996 interpretation of possible biogenic activity within the

meteorite has been strengthened. All of the criticism offered to date may attack single points within our model but they cannot account for the multitude of interesting phenomena within the sample.

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THE SEARCH FOR LIFE ON MARS

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A comprehensive understanding of the origin and nature of life will ultimately require knowledge derived from non-terrestrial, as well as terrestrial, life. Although it is likely that life is widespread in the universe, technical limitations currently restrict our search for extraterrestrial life to regions relatively close to the Sun. Of the potential habitats presently known, none is more accessible than Mars. Also, because environments on Earth and Mars were quite similar 3.5-4 Gyr ago, when life was emerging on Earth, and because terrestrial life emerged very rapidly once conditions permitted, emergence of life on Mars at that time seems quite plausible. Given that planet's presently hostile surface environment, detection of any possible extant martian life represents a formidable technical challenge, but an active search for evidence of an extinct biota is scientifically and technically feasible /1/. Furthermore, even if life never began on Mars, any record of prebiotic chemical evolution preserved in martian rocks would greatly enhance our understanding of such processes on Earth, where the record of that epoch has been thoroughly destroyed.

The criteria to be satisfied for general acceptance of evidence of life, extant or extinct, on Mars will be severe. The geochemical, mineralogical and morphological observations recently reported by McKay et al. /2/ for the martian meteorite ALH84001 fail to meet those criteria. It is unlikely that study of any known martian meteorites will improve upon this situation. A viable search for evidence of ancient life on Mars will require a sequence of robotic-spacecraft missions, culminating in return of carefully selected samples to Earth. By analogy with the record of early terrestrial life, those samples will be aqueously deposited sedimentary rocks containing organic matter. Key to successful sample return will be a series of precursor missions capable of, first identifying promising landing sites from orbit, and second identifying promising rocks at such a site. Only modest enhancement of currently planned orbital missions will be required, but considerable development of lander spacecraft will be needed, particularly with regards to mobility on, and ascent capability from, the martian surface. A realistic time frame for an exobiologically optimised Mars sample return mission is probably about 2009. Presently unanticipated discoveries may permit an earlier mission, but otherwise an accelerated program would be much less likely to succeed scientifically.

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RADAR DETECTABILITY OF A SUBSURFACE OCEAN ON EUROPA

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The initial reconnaissance of the jovian system by the Voyager spacecraft and models of tidal heating of natural satellites suggested the possibility of a liquid water ocean beneath the ice of Jupiter's moon Europa. Recent high resolution imaging of Europa from the Galileo spacecraft is consistent with this interpretation, and suggests that in some locations, liquid water may lie within a few kilometers of Europa's surface. Since liquid water is essential for life as we know it, the possible existence of a second liquid water ocean in the solar system is of great exobiological interest. In addition, a subsurface European ocean may provide a model for the early Earth at the time of the terrestrial origin of life. The search for and initial characterization of a European ocean, most likely via an orbiting spacecraft, is now one of the highest priority objectives of solar system exploration.

An orbiting radar sounder may be able to detect directly the presence of a subsurface European ocean. The radar detectability of the putative ocean depends on the transparency of the overlying ice, which in turn will depend on the ice's purity and temperature gradient, as well as the radar wavelength. Here we demonstrate that consideration of those factors plus available constraints on the properties of European ice places a limit of about ten kilometers on the depth to which an ocean might be detectable with an orbiting radar.

EARLY LIFE ENVIRONMENTS ON EARTH AND MARS (ELEEM)

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To evaluate model experiments seeking to reconstruct the sequence of events that led to the synthesis of biomolecules and ultimately to the origin of life itself, it is necessary to examine the geological record. This record in the oldest sediments on Earth is the only source of information available about the physical chemical conditions (e.g. temperature, ocean pH, impacts, atmospheric composition, life) present at the surface of the Earth at the time of the emergence of life before ca. 3900 Ma /1,2/.

Rocks of the Isua region in southern Greenland, are contained within extensive amphibolite to granulite facies granitoid gneisses of early Archean (3600-3900 Ma) age. The identification of water-lain sediments such as banded iron-formation (BIF), metachert, and pillow lava basalts in these ancient rocks attests to the presence of a developed marine sedimentary system by ~3900 Ma /3/. Recent carbon isotope studies on carbonaceous inclusions within apatite (basic calcium phosphate) grains >from early Archean, Proterozoic and younger sediments up to presently forming marine deposits, have demonstrated strongly negative (i.e. "isotopically light") isotope values of the carbon. Such isotopically light carbonaceous matter is consistent with a bioorganic origin, and this finding has been extended to the oldest known sediments which are ≥ 3850 Ma /3/. The $\delta^{13}\text{C}$ values measured on the inclusions collected from the Isua supracrustal belt (ISB) of West Greenland (weighted mean: -30%) and a ≥ 3850 Ma BIF /3/ from Akilia island (weighted mean: -37%) deviate from the $\delta^{13}\text{C}$ values reported previously in the majority of whole-rock reduced carbon >from the ISB.

Biopoesis on Earth must have substantially pre-dated this earliest appearance of life at ~3900 Ma /2/. The ancient surface of the planet Mars probably holds clues to the nature of the earliest environments for the emergence of life. The search for the occurrence of phosphate minerals and possible associations of isotopically fractionated carbon as applied to ancient terrestrial sediments, is part of the exobiological search plan for Mars exploration and sample return, and for examination of the martian meteorites /4/.

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IN VITRO EVOLUTION OF NOVEL RNA AND DNA ENZYMES

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The principles of Darwinian evolution can be applied to a large, heterogeneous population of RNA or DNA molecules to obtain particular molecules that have desired biochemical properties, including the ability to catalyze a target chemical reaction. A population of variant molecules is subjected to repeated rounds of selective amplification in the test tube. Only those individuals that perform a chosen catalytic task are amplified so that, through successive rounds, the population adapts to the task at hand.

Recently we developed the ability to carry out the *in vitro* evolution of RNA-based catalytic function in a continuous manner. The RNAs catalyze a ligation reaction that immediately makes them eligible for amplification and the newly-produced RNAs are immediately eligible to catalyze another reaction. This has enabled us to maintain laboratory "cultures" of evolving RNA enzymes, analogous to the way one maintains cultures of bacteria. The RNAs are perpetuated by a simple serial transfer procedure, amplifying indefinitely so long as an ongoing supply of substrate and other reaction materials is made available. During one run of continuous *in vitro* evolution, the RNA enzymes were amplified by a factor of 10^{298} over 52 hours. By the end of this process, new "generations" of progeny RNA molecules were being produced approximately every 5 minutes.

We used stepwise *in vitro* evolution to develop a DNA enzyme that promotes the formation of a peptide bond between an aminoacyl-oligonucleotide and a peptidyl-oligonucleotide, both bound via their oligonucleotide components at adjacent positions along a complementary template. The reaction format is analogous to that of the peptidyl transferase center of the ribosome, but the chemistry is more akin to the biosynthesis of microbial peptides, involving attack of the α -amine of an amino acid on the carbonyl carbon of a thioester-linked peptide.

CHEMISTRY OF THE BIOGENIC ELEMENTS IN DENSE INTERSTELLAR CLOUDS AND RELATIONS TO THE SOLAR SYSTEM

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The basic theme of this program is the study of molecular complexity and evolution in interstellar clouds, and the relation of this chemistry to that in primitive solar system objects such as comets. This research includes the identification of new molecular species in both environments and the probing of chemical processes from accurate determination of molecular abundances. Such investigations provide essential boundary conditions for the subsequent evolution of biogenic compounds in the solar nebula and during planetary formation. The research emphasizes observations of the pure rotational spectra of molecular species at submillimeter and millimeter wavelengths, which provide powerful means of probing the physics and chemistry of the gas phase.

Recent research on dense interstellar clouds includes the identification of two new interstellar molecules, ethylene oxide ($c\text{-C}_2\text{H}_4\text{O}$) and the protonated formaldehyde ion (H_2COH^+), and a comprehensive analysis of the interlinked chemistry and physics of two dark molecular clouds, TMC-1 and L134N. Ethylene oxide is only the third cyclic species unambiguously detected in the interstellar medium. It is a higher energy isomer of the known interstellar species acetaldehyde (CH_3CHO) and of the as yet undetected molecule vinyl alcohol (CH_2CHOH). The high abundance of $c\text{-C}_2\text{H}_4\text{O}$ and CH_3CHO relative to gas phase chemical models suggests that their production involves grain-mediated processes. For the dark cloud study emission from 34 transitions of 22 molecular species and isotopomers was mapped in two clouds of similar physical but differing chemical properties. This large data set allowed consistent determinations of temperature, density and chemical composition, and the spatial gradients in these quantities.

The recent apparitions of Comets Hyakutake and Hale-Bopp provided a spectacular opportunity to study cometary physics and chemistry, and possible links between interstellar and cometary material. Important results include the first detection of cometary HNC (hydrogen isocyanide) and the first detailed mapping of HCN and HCO^+ in cometary comae. The HNC/HCN abundance ratio is vastly higher than that predicted by equilibrium chemistry, and is similar to values found in the interstellar medium. The possibility that Cometary HNC includes preserved interstellar matter is being investigated by analyzing the HNC/HCN ratio versus heliocentric distance.

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PHOTOCHEMICAL EVOLUTION OF THE BIOGENIC ELEMENTS IN PRE-COMETARY/INTERSTELLAR ICE ANALOGS

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During the past two decades ground-, air-, and space-based infrared spectroscopic observations combined with realistic laboratory simulations have revolutionized our understanding of interstellar ice and dust, the raw materials from which planets, comets and stars are formed. Understanding the chemical composition of this feedstock provides insight into the nature of the material brought into the inner parts of the Solar System by comets and meteorites.

Most interstellar material is concentrated in large molecular clouds where simple molecules are formed by dust grain and gas phase reactions. Gaseous species striking the cold (10° K) dust will stick, forming an icy grain mantle. This accretion, coupled with energetic particle bombardment and UV photolysis, will produce a complex chemical mixture containing volatile, non-volatile, and isotopically fractionated species. Ice species identified in molecular clouds include H₂O, CH₃OH, CO, CO₂, and H₂ as well as nitriles and ketones or esters. During the past three years we have added several new species to this list. This evidence, and the resulting photochemistry will be summarized, emphasizing the potential prebiotic role of some of these species. The ready formation of complex organic species from simple starting mixtures under interstellar conditions and the ice chemistry that ensues when these ices are mildly warmed suggest that comets may have played an important role in the origin of life.

IS MOTHER EARTH THE MOTHER OF LIFE? THE SEARCH FOR ORGANIC MOLECULES INSIDE MINERALS AND ROCKS

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We explore the possibility that complex oxygenated organic molecules can be formed inside the hard, dense matrix of magmatic minerals from dissolved H₂O and CO₂. The theoretical basis of our work is well understood. When H₂O and CO₂ become incorporated as "impurities" in minerals crystallizing in H₂O and CO₂-laden environments, they undergo an internal redox conversion by which they split off H₂ and reduced C. Such H₂ and C behave as "impurities" and segregate upon further cooling to dislocations and other major defects. There, C-C and C-H bonds begin to form, building the backbones of what will become organic molecules when the minerals are weathered.

To simulate weathering we start from upper mantle 10-20 mm large, gem-quality olivine single crystals. We clean them with chloroform and then crush them to a medium fine powder which is then subjected to a H₂O Soxhlet extraction. The organics thus obtained are analyzed by GC-MS, using standard tert-Butyldimethylsilyl (t-BDMS) derivatization. One everlasting concern is contamination. We therefore expanded our study to the vesicular basalt that had brought the olivine crystals from mantle depth during a volcanic eruption. The rationale was that, if adventitious contamination occurred from biogenic sources, the basalt would be much more receptive than the gem-quality olivine crystals. The basalt was treated and extracted in exactly the same way.

While the basalt was essentially devoid of extractable organics, the olivine crystals yielded a rich spectrum of compounds. This includes aliphatic monocarboxylic acids, H₃C-(CH₂)_n-COOH with n ranging from 6 to 10, and an N-bearing compound, C₂H₃NO₂, most likely glycolamide. Other compounds seen in the GC-MS data set still await identification. To our knowledge this is for the first

time that fatty acids have been identified in extracts from olivine crystals from the upper mantle. Glycolamide had been reported by George and Cronin (1994) from Murchison meteorite.

An extraneous source of the organics can be ruled out. We conducted full procedural blanks and controls with the vesicular basalt from the same locality. Given the gem quality of the olivine crystals plus the fact that the basalt yielded nil organics, we can dismiss the hypothesis by Tingle, Mathez, and Hochella (1991) that the volcanic gases catalyzed organics by reacting with exposed surfaces and micro-cracks which opened and closed during the eruption.

The chain molecules extracted from the olivine crystals suggest that the C_n backbones form by solute C segregating into dislocations. These are 1-dimensional defects and act as trapping sites for "impurities" in the mineral matrix. Minerals have an assortment of 1- or 2-dimensional defects. If they all act as trapping sites for C_n backbones, the molecules to be released through weathering are expected to belong to a select group of stereochemically restrained compounds. Massive weathering of mafic/ultramafic rocks on the early Earth may have provided a source of such compounds – for the benefit of our Life. On other planets with tectonics and surface water, similar weathering processes are expected to provide similar organic compounds – for the benefit of their Life.

MOLECULAR MODELING OF PROTOCELLULAR STRUCTURES AND FUNCTIONS

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Even the simplest protocell must have had the capability to catalyze the chemical reactions needed for its survival and growth, capture and utilize energy, and communicate with its environment. These functions must have been accomplished by simple molecules present in protobiotic milieu. One such group of potential early catalysts and signaling molecules were peptides - likely precursors of enzymes and receptors. Unfortunately, most short peptides are disordered in aqueous solution and, therefore, do not appear suitable for performing cellular functions. However, many of these peptides, depending on their sequence, can acquire a broad range of well defined secondary structures, such as α -helix and β -strand, at water-membrane, water-oil or water-air interfaces. A crucial, common characteristic of these interfaces is that a nonpolar phase is adjacent to water.

The organization of small peptides at aqueous interfaces, essential for catalytic activity and signaling, was examined in large-scale molecular dynamics simulations of several peptides composed of two amino acids, nonpolar leucine (L) and polar glutamine (Q). Based on results for the LQQLLQL heptamer, designed to maximize interfacial stability of an α -helix by exposing polar side chains to water and nonpolar side chains to a nonpolar phase, it is proposed that, whenever possible, peptides fold at interfaces through a series of amphiphilic intermediates. Once folded, the peptides form structures that are suitable for polymerization and have potential for catalytic activity.

If peptides consist of nonpolar residues only, they insert into the nonpolar phase. As demonstrated by the example of the leucine undecamer, such peptides fold into an α -helix as they partition into the nonpolar medium. The folding proceeds through an intermediate, called 3_{10} -helix, which remains in equilibrium with the α -helix. Once in the nonpolar environment, the peptides can readily change their orientation with respect to the interface from parallel to perpendicular, especially in response to local electric fields. The ability of nonpolar peptides to modify both the structure and orientation with changing external conditions may have provided a simple mechanism of transmitting signals from the environment to the interior of a protocell.

Another protocellular function the mechanism of which has been studied using molecular modeling is the activated formation of transmembrane proton gradient. This gradient could have driven chemical synthesis in the protocell. A simple, peptide-based model of a transmembrane proton pump consists of a proton source and two acceptors. The directionality of the pump is ensured by a "gate-keeping" mechanism involving a water molecule, conformational change of the primary acceptor or tautomerization of a histidine. The pump can be formed by two transmembrane peptide helices but not one helix.

STRUCTURE AND FUNCTION OF ENCAPSULATED REPLICATING SYSTEMS

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The origin of cellular life necessarily involved the self-assembly of relatively simple organic molecules into more complex membranous structures. Liposomes can be used to model this process, particularly in the form of catalytic macromolecules encapsulated within lipid bilayer vesicles to produce simple cellular structures. We have established two encapsulated polymerase systems that can incorporate external substrates to synthesize nucleic acids in the internal volume. In the first, a lipid with relatively short chains is used to prepare liposomes containing polynucleotide phosphorylase. Under these conditions the enzyme is captured within the lipid vesicles, but the bilayer is sufficiently permeable to allow a substrate like ADP to cross into the liposome, so that RNA is synthesized by the polymerase (Chakrabarti et al. 1994).

We are now attempting to extend this result to a template-dependent process involving T7 RNA polymerase. This enzyme synthesizes RNA using a DNA template and four nucleoside triphosphates (NTPs). It should be possible to capture both the polymerase and a template in a liposome, supply substrate and primer, and demonstrate the synthesis of RNA complementary to the template. However, we found that considerably higher permeability of the lipid vesicles is required for the reaction to proceed at useful rates. We are therefore exploring methods by which permanent pore-like structures can be introduced into lipid bilayers. One such pore is produced by alpha hemolysin, a bacterial toxin that self-assembles as heptamers in lipid bilayers to form a 2.2 nm transmembrane channel (Song et al. 1996). We have found that the alpha hemolysin channel produces pores in lipid bilayers that can accommodate high fluxes of ionic nucleotides. Surprisingly, single strands of RNA or DNA up to 1000 nt in length can also pass through the channel (Kasianowicz et al. 1996). In preliminary experiments we have had modest success in synthesizing RNA with encapsulated polymerase, using the pore to transport NTP substrates at sufficient rates to support the polymerase activity. This system represents a model for the first forms of cellular life, and its properties provide information about the hurdles that were overcome by complex self-assembled molecular systems on the evolutionary path to the first cells.

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PHOTOSYNTHESIS AND IRON IN HIGH IRON MICROBIAL MATS

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Photosynthesis evolved early in the history of life on Earth and had major environmental impacts locally and globally. Many different forms of photosynthesis exist on Earth today and the origin and evolution of these forms is relevant to understanding some of the major events and environmental impacts of photosynthesis on the history of life and the planet itself. The direct photo oxidation of iron (photoferrotrophy) is one of the forms of photosynthesis that may have preceded the evolution of oxygenic photosynthesis. Anoxygenic photoferrotrophs have recently been detected but their relationship to the ancient emergence of oxygenic photosynthesis and their environmental impacts are yet to be determined. Understanding the roles of photoferrotrophs and oxygenic phototrophs in the oxidation of, precipitation of, and deposition of iron is important in interpreting the origin of oxidized iron in the early history of Earth and possibly on Mars. We are studying a thermal iron spring in Yellowstone National Park to determine the relationships of all of the phototrophs to the oxidized iron accumulations and to seek additional types of photoferrotrophs. It may be possible to find a biological signature in these iron deposits that could be preserved over geologic time.

Oxygenic cyanobacteria are abundant in the iron deposits at Chocolate Pots hot springs. The anoxic source waters contain about 9 mg/L ferrous iron and 1.0 mg/L Mn. Four different communities are present over a temperature range of 56 to 30° C. Dominant filamentous forms appear to have a role in stabilizing the otherwise flocculant iron oxide/hydroxide precipitates. This stabilizing influence may contribute to the building of the deposit. Microelectrode studies reveal that the oxygenic activity of the cyanobacteria greatly increases the level of oxygen in the sediment/water interface to values as high as 200% saturation. Their autotrophic activity raises the pH substantially from around 7 (in the water) to over 9 during daylight in the top two mm of sediment. At night oxygen falls to below saturation values at the interface and to zero within a mm of the sediment surface. pH values also fall at night. The photosynthetic activity of two of the cyanobacterial communities is substantially increased in the presence of 1.0 mM Fe(II) although direct photoferrotrophy has not yet been demonstrated.

SPECIES COMPOSITION OF HOT SPRING CYANOBACTERIAL MATS

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Modern microbial mats are studied as analogs of stromatolites, the predominant surviving fossils of Precambrian microbial life. Mats which occur in hot springs are among the best-studied model systems—understanding them gives insight as to the composition, structure and function of microbial communities that might have once predominated Earth's biota, and consequently its biogeochemistry. Limitations of traditional microbiological methods, such as microscopy and cultivation, have impaired our ability to even understand which microbial populations comprise such microbial communities. However, new molecular tools are enabling us to vastly improve our ability to detect the native populations that inhabit these mats, and to understand their ecology and evolutionary history. This knowledge is, in turn, helping us to better understand what prokaryotic species are, and the evolutionary processes that explain their biodiversity and ecological significance within and among modern mat communities.

We have focused on cyanobacterial populations inhabiting the mat in Octopus Spring, Yellowstone National Park. The simple morphology of the unicellular cyanobacteria (genus *Synechococcus*) dominating this mat, combined with the overly selective pressure of culture methods, masks a

remarkable diversity of cyanobacterial populations which are defined by unique 16S rDNA gene sequences. Because they exhibit unique ecological patterns of occurrence relative to environmental gradients, these populations can be considered as unique species, provided that we abandon the arbitrary concept of procaryotic species microbiologists usually use and replace it with the more ecological view of species used by macrobiologists. The close genetic similarity among many of these cyanobacterial species challenges us to consider whether 16S rDNA sequences are themselves too conserved to detect individual species. We have begun to reveal genetic diversity within 16S rDNA-defined populations, by examining sequences in the intervening transcribed spacer region separating 16S and 23S rDNA genes.

BIOGEOCHEMISTRY OF CARBON IN THE ANCIENT BIOSPHERE: PERSPECTIVES FROM MODERN MICROBIAL COMMUNITIES AND THE ANCIENT CARBON ISOTOPIC RECORD

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The geologic record allows us to describe early habitable environments and to compare the timing of environmental change and biological innovations. The $\delta^{13}\text{C}$ values of organics and carbonates reflect the processing of C within organisms and ecosystems; and these $\delta^{13}\text{C}$ values can be retained in ancient kerogens and carbonates. However, this $\delta^{13}\text{C}$ record is a product of the entire array of processes and reservoirs that define the biogeochemical C cycle. Thus the fullest interpretation of the $\delta^{13}\text{C}$ record will be achieved only through a balanced approach to deciphering the history of the entire C cycle.

Ecological processes affect organic $\delta^{13}\text{C}$ values of microbial mats. As the fraction of organic C decomposed by sulfate reduction increased, relative to the rate of aerobic decomposition, secondary production by aerobic sulfide oxidizing chemoautotrophs became a larger fraction of primary production. Discrimination by sulfide-oxidizers was large, at times lowering mat $\delta^{13}\text{C}$ values by as much as 8 per mil. This finding, which is analogous to a model proposed by J. Hayes for isotopic discrimination within a methanogen/methanotroph cycle during the late Archean, indicates that organic $\delta^{13}\text{C}$ values can be lowered substantially by secondary production in a microbial ecosystem. This secondary production can be sustained by oxidation either of organic C or sulfur substrates.

In Green Lake, NY, blooms of *Synechococcus* sp. dominate the precipitation of micritic carbonate which exhibits $\delta^{13}\text{C}$ values as much as 4 per mil larger than the $\delta^{13}\text{C}$ of lake water dissolved inorganic C (DIC). Micritic carbonate precipitates under highly alkaline conditions within and adjacent to extracellular organic "S layers, where the $\delta^{13}\text{C}$ of DIC is elevated due to isotopic discrimination during photosynthetic assimilation of C.

Post-depositional thermal alteration degrades kerogens, lowering elemental H/C and increasing $\delta^{13}\text{C}$ in residual kerogen. A plot of H/C versus $\delta^{13}\text{C}$ for a large data set of Proterozoic kerogens can indicate the magnitude of this $\delta^{13}\text{C}$ shift, if the time interval sampled witnessed no large long-term changes in kerogen $\delta^{13}\text{C}$ values. Independent plots for mid-Proterozoic and Neoproterozoic kerogens both indicated that $\delta^{13}\text{C}$ values were between 2 to 2.5 per mil more positive in kerogens with H/C values of 0.2, relative to kerogens with H/C of 0.8. Thus the thermal alteration of kerogen $\delta^{13}\text{C}$ values has been considerably lower than had been estimated previously.

THE DISTRIBUTION OF PROTEROZOIC FOSSILS IN TIME AND SPACE

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We know, and have known for decades, that Phanerozoic ecosystems were preceded by a long interval of Precambrian evolution. The biology of Archean oceans remains poorly constrained, but in recent years, taxonomic, paleoenvironmental, and stratigraphic patterns have emerged that enable us to approach the Proterozoic fossil record in a predictive fashion that looks to generalizations about early life.

Cyanobacteria are among the most morphologically diverse and developmentally complex of all eubacteria, making them one bacterial clade for which morphology provides useful systematic characters. Cyanobacteria were widely distributed in Proterozoic environments favoring fossil preservation; fossil taxa show consistent patterns of paleoenvironmental distribution within a time interval, as well as stratigraphic distributions that mirror those of sedimentary and geochemical indices of Earth's environmental development. Even shallow branches of the cyanobacterial tree, including the heterocyst-bearing Nostocales, are represented in fossil assemblages 2100 Ma or older, indicating that much cyanobacterial diversification occurred during the Archean or earliest Proterozoic Eon.

Eukaryotes are represented in Proterozoic rocks by both morphological and biomarker remains. Although simple microfossils and steranes of probable eukaryotic origin can be traced back to 1800 Ma and possibly as far as 2450 Ma, there is little evidence for pronounced algal diversification until about 1200 Ma, when green, red, and chromophyte algae first appear in the record. Much of the ordinal-level diversity architecture of these algal groups was already in place by the time that diverse Ediacaran fossils first appear in the geological record.

THE BIOLOGICAL POTENTIAL OF MARS (AND MARS MISSIONS)

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Possible biological activity on Mars has been postulated on the basis of martian environmental conditions meeting those necessary for an origin and continued existence of life. Based on the terrestrial example, these conditions include: i) the existence of liquid water at the surface or in the subsurface throughout geologic time, ii) the availability and accessibility of the biogenic elements, and iii) a source of energy to drive the system out of chemical equilibrium, with the movement back toward equilibrium providing energy for biota. Two aspects of this that have not been addressed in detail include the availability of chemical energy to power life and the ability to find suitable locations on the martian surface. Both of these are of significance in planning future missions to Mars that will search for life.

Although it is difficult to estimate the total chemical energy available on Mars and the efficiency with which it can be accessed, we can use simple scaling arguments to compare available energy with the Earth. Assuming that early life got its energy from chemical energy obtained through hydrothermal systems, the total amount of energy available is proportional to the total volume of volcanic materials. Both instantaneously and integrated over time, Mars had about 1% the total volcanic eruption rate as Earth. This means that the energy available on Mars in 4 billion years is equivalent to the energy available on Earth in only 40 million years. If the propagation of life is energy limited, then Mars may have contained no more life than was present on Earth after only 40 m.y. Of course, this comparison

assumes that all other factors don't matter; they do, although this calculations provides a basis for quantitative comparison of martian and terrestrial life.

We can use Mars Pathfinder results to estimate the properties of sites that may contain fossil or extant life. The Pathfinder site showed evidence at the surface for the same geological processes as have acted at the larger scale seen from orbit. This is fundamentally different from the two Viking sites, where there was no evidence at the ground for the same processes having acted, and the sites appeared to consist only of rock, dust, crust, etc. This suggests that the geologically interesting sites (not covered by dust) will show features resulting from the same processes that make them interesting – for example, a volcanic site will look like a volcanic site from the surface. Unfortunately, this means that rover traverses will be much more difficult than envisioned based only on the Viking data. Traverses of several tens of kilometers may not be possible for some of the most interesting sites.

THE NASA SPECIALIZED CENTER OF RESEARCH AND TRAINING (NSCORT) IN EXOBIOLOGY

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The NSCORT/Exobiology program was initiated in January, 1992 and funded for five years. We recently competed for a five year renewal, and this renewal was awarded effective April, 1997. The NSCORT/Exobiology program has an annual budget of approximately \$1,000,000, and in the five year renewal the number of PIs has increased from five to six, and an Outreach Coordinator (Wills) has also been added.

The continued major function of the NSCORT is to train young scientists in the field of Exobiology. Thus, the bulk of the \$1,000,000 annual budget is used to support the research and training of undergraduate, graduate and post-doctoral Fellows who are selected on a competitive basis. About five Fellows at each level are supported each year. The goal of our training program is to produce the next generation of young scientists needed to carry out cutting edge research in the areas relating to the origin of life and exobiology.

The NSCORT/Exobiology research program addresses the central issue of the origin of life: the nature of the first genetic material. The first appearance of a molecular system that could store information and replicate imperfectly marked the transition from the abiotic chemistry of the primitive Earth to biochemical evolution. The projects of the various PIs constitute a concerted effort to investigate all aspects of the chemistry that led to the origin and evolution of the first self-replicating systems and how these systems eventually evolved into the biochemistry associated with modern day organisms.

A vigorous Exobiology outreach program (annual budget = \$25,000) involving the scientific community, K-12 and college students and teachers and the general public is supported by the NSCORT. An Internet site (address, <http://www.chem.ucsd.edu/~nscort/NSCORT.html>) describes the NSCORT activities, research programs and Fellowship opportunities. The 1999 meeting of the International Society for the Study of the Origin of Life (ISSOL) will be hosted by the NSCORT in La Jolla.

ENANTIOMERIC EXCESSES IN THE AMINO ACIDS OF CARBONACEOUS CHONDRITES

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The organic matter of carbonaceous chondrites is representative of that fraction of the early Earth's total organic matter delivered by the fall of such meteorites and perhaps interplanetary dust. Consequently, it may provide insights to chemical evolution and the origin of life. Enantiomeric ratios of chiral organic compounds in these meteorites have been of interest for many years because they offer a way to assess terrestrial contamination. Furthermore, the finding of enantiomeric excesses (ee) not related to contamination suggests that an asymmetric influence was manifest in chemical evolution and may have played a role in the origin of the homochirality that characterizes terrestrial life.

Our recent finding /1/ of small L-ee in both of the two enantiomeric pairs of 2-amino-2,3-dimethylpentanoic acid (DL- α -methylisoleucine and DL- α -methylalloisoleucine) and two other α -methyl amino acids, isovaline and α -methylnorvaline, obtained from the Murchison meteorite has now been confirmed in preparations of these amino acids from the Murray meteorite. As in Murchison, the α -hydrogen analogues of the latter amino acids, α -amino-*n*-butyric acid and norvaline, were found to be racemates. The L-excesses found for the enantiomeric pairs of 2-amino-2,3-dimethylpentanoic acid from Murray were smaller than those found for their Murchison analogues. In addition, L-excesses were observed in Murray for two other amino acids, α -methylvaline and α -methylnorleucine.

We did not observe the substantial excess of L-alanine reported by others /2/ in our fractionated Murray extract. Without prior fractionation on a reverse-phase column, several other amino acids with similar retention times are present in carbonaceous chondrite extracts and can interfere with determination of the alanine enantiomer ratio.

Attempts to extend these observations to other classes of chiral organic compounds are underway, but in some cases (amines, hydroxy acids) suitable analytical methods have proved difficult to establish.

The hypothesis /3/, that enantiomeric excesses might originate from exposure of planetary or interstellar organic matter to a flux of circularly polarized light (CPL) of a specific handedness produced as synchrotron radiation by neutron stars, is an attractive explanation for the ee observed in meteorite amino acids. This hypothesis predicts that the less abundant enantiomer in all cases (D) will preferentially absorb CPL of a particular handedness. Stereospecific syntheses of the meteoritic amino acids showing ee are being carried out with the intent of measuring their circular dichroism spectra.

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MODIFICATION OF AMINO ACIDS AT SHOCK PRESSURES OF 3.5 TO 32 GPa

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The majority of meteorites studied today are thought to originate in the asteroid belt. Impacts among asteroidal objects generate heat and pressure that may have altered or destroyed pre-existing organic matter in both targets and projectiles to a greater or lesser degree depending upon impact velocities. Dynamical models of asteroid evolution suggest relative velocities quite low initially, but rising to a maximum of about 5 km/s which corresponds to a shock pressure of ~30 GPa. Very little is known about the shock modification of organic matter relevant to this stage of the cosmic history of biogenic elements and compounds or to impacts on early Earth. Our study describes the effects of impacts on selected classes of organic compounds utilizing laboratory shock facilities. Amino acids were subjected to shock impact over a pressure range of 3.5 to 32 GPa both within and without meteoritic mineral matrices. The extent of amino acid destruction, racemization, and conversion to secondary amino acids was examined. Abundances of parent compounds decreased by a factor of 10^3 over this range. Racemization also occurred, but some residual optical activity remained in the amino acids surviving shocks up to 32 GPa. Secondary amino acids formed in the high peak pressure range; those identified were β -alanine, glycine, alanine, γ -aminobutyric acid, and β -aminoisobutyric acid. At 30 GPa, the abundances of these daughter compounds exceeded those of the remaining initial amino acids. As the concomitant effects of high mechanical stress and temperature accompanying shocks cannot be separated in this work, their relative contribution to the observed transformations cannot be estimated. Amino acid survival in shock experiments suggests that, after formation/emplacement of amino acids in carbonaceous chondrite parent bodies, these objects never experienced impact velocities >5 km/s, which suffices to generate 30 GPa for typical silicate/silicate impacts. Notably, fragments of Canyon Diablo meteorite recovered from Meteor Crater, Arizona, are reported to have suffered shocks of <13 GPa. Our results suggest that if the Canyon Diablo event was typical of asteroidal impactors striking Earth at ~14 km/s, some small fraction of the organic compounds contained within such projectiles, even amino acids, would have survived intact.

AN INVESTIGATION OF SUGARS AND OTHER POSSIBLE FORMALDEHYDE PRODUCTS IN THE MURCHISON METEORITE

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Carbonaceous meteorites are of interest in the study of early solar system organic chemistry and the origin of life. This is due to their pristine nature, age (~4.5 billions years), and abundance of organic compounds. Because of the past and present delivery of meteoritic material to the Earth and other solar system bodies, carbon and organic compounds were available for prebiotic chemistry. The Murchison meteorite, the best characterized carbonaceous meteorite with respect to organic chemistry, contains numerous compounds of potential prebiotic importance. These include amino acids, amides, carboxylic acids, hydroxy acids, sulfonic acids, phosphonic acids, purines and pyrimidines. Notably absent among the biologically important compounds reported in Murchison are polyhydroxylated compounds, polyols, including sugars (polyhydroxy aldehydes or ketones). Ribose and deoxyribose, which are five carbon sugars, are essential components of contemporary nucleic

acids, DNA and RNA. If polyhydroxylated compounds are shown to be indigenous to meteorites, this would demonstrate that such compounds were abiotically synthesized at the beginning of the solar system and therefore could have been part of the initial mixture of compounds available for the origin/evolution of life on the early Earth. The objectives of this project are to determine the abundance, structure, and origins of polyhydroxylated compounds in the Murchison meteorite. The procedures used include gas chromatography-mass spectrometry and isotope-ratio mass spectrometry.

One of the most generally agreed upon routes for the prebiotic synthesis of polyols is the "formose" reaction. In this reaction, formaldehyde (CH_2O) in slightly basic aqueous solution reacts with itself to gradually build a variety of hydroxylated compounds and sugars of increasing carbon number. Because there was aqueous alteration on the Murchison parent body, and simple carbonyl compounds are constituents of Murchison, this reaction would have been possible. Our preliminary analysis of Murchison extracts suggests at least a partial product distribution of a formose-like reaction. Thus far we have identified ethylene glycol, glycerol, dihydroxyacetone, glyceric acid, and other possible polyols. Preliminary isotopic measurements of bulk samples also indicate that the majority of Murchison polyols are indigenous to the meteorite. Isotopic measurements (D/H , $^{13}\text{C}/^{12}\text{C}$, and $^{16}\text{O}/^{17}\text{O}/^{18}\text{O}$) of individual compounds will help to determine their origins as well as if they are indigenous.

CO-ORIGIN OF METABOLISM AND BIOPOLYMER SYNTHESIS USING FORMOSE SUGAR SUBSTRATES

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Modern life can be described as a complex chemical process (metabolism) that is catalytically controlled by its products (proteins-nucleic acids) in a way that enhances the perpetuation of the entire system. Consequently, the origin of life can be described as a continuous series of events in which a prebiotic chemical process came increasingly under the control of its catalytic products. In our search for this prebiotic process (earliest metabolism) that yielded catalytic take-over products (such as polypeptides), we have investigated – (a) the thermodynamics of the reactions of carbon groups in order to establish the general principles (a historical thermodynamic constraints) that govern modern metabolism and chemical processes involved in its origin, and (b) the chemistry of laboratory models of prebiotic processes that could have been involved in the origin of metabolism and biopolymer synthesis. These studies of the chemical transformations of carbon point to sugars as the optimal substrates for the co-origin of metabolism and biopolymer synthesis.

To better understand the energetics of prebiotic and biotic carbon chemistry, we examined the relationship between redox disproportionation of carbon substrates and the free energy change of biosynthetic and fermentative pathways. Redox disproportionation is defined as the transfer of electrons between two carbon groups that results in an increase (by 4 oxidation number units per 2 electrons transferred) in the distance separating the two carbon groups on the oxidation number scale of carbon. This study showed that in *E. coli*, redox disproportionation of sugar carbon accounted for 84% and 96% (and ATP only 6% and 1%) of the total energy amino acid and lipid biosynthesis, respectively. Redox disproportionation of carbon, and not ATP, is the primary energy source driving amino acid and lipid biosynthesis from glucose. Because disproportionation energy is determined by the invariant half-cell reduction potentials of carbon groups, and since sugars have the highest energy yield of multi-carbon substrates, sugars can be considered the universal optimal biosynthetic substrate.

Since thermodynamic instability of sugars also makes them attractive prebiotic substrates, we are currently investigating the prebiotic synthesis of "activated" amino acid thioesters and peptides from formaldehyde-derived sugars and ammonia in the presence of thiols under mild aqueous conditions. We recently demonstrated that alanine and homoserine are synthesized from formaldehyde, glycolaldehyde (substrates of the formose autocatalytic cycle) and ammonia in the presence of thiol catalysts. This 'one-pot' thiol-dependent prebiotic synthesis presumably yields amino acids via amino acid thioester intermediates that can form peptides. This prebiotic synthesis, which models both metabolism (glycolysis) and biopolymer synthesis (protein synthesis) uses the same redox engine as modern glycolysis and amino acid biosynthesis. We are also examining possibility that this chemical process generates autocatalytic products by using selection techniques to evolve the system in a way that increases its production of autocatalytic products (rudimentary molecular replicators).

THE ORIGIN AND EVOLUTION OF OXYGENIC PHOTOSYNTHESIS

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The advent of oxygen evolving photosynthesis is one of the central events in the development of life on Earth. Prior to the evolutionary origin of this metabolic capability, the atmosphere of the early Earth was largely anaerobic. The development of more advanced eukaryotic life forms did not take place until the free oxygen level in the atmosphere rose to a sufficient level. While significant questions remain over the timing of the beginning of oxygenic photosynthesis, no other process, either biogenic or nonbiogenic, is capable of producing the large quantities of molecular oxygen that demonstrably changed the course of life on Earth. Understanding the evolutionary origin of this metabolic process is therefore of considerable importance.

The evolutionary developments that led to the ability of photosynthetic organisms to oxidize water to molecular oxygen are discussed. Two major changes from a more primitive reaction center are required, a charge accumulating system and a more oxidizing reaction center pigment. Intermediate stages are proposed in which hydrogen peroxide was oxidized by the reaction center and an intermediate pigment similar to chlorophyll *d* was present.

HORIZONTAL GENE TRANSFER: PITFALLS AND PROMISES

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Phylogenetic reconstruction from protein or nucleic acid sequence families at best provides information on the evolution of individual genes. In contrast to the assumed tree-like evolution of genes, organismal evolution is characterized by the exchange of genetic information between organisms and even by the fusion of formerly independent lines of descent. Horizontal gene transfer often has been regarded as a last ditch attempt by systematists to reconcile controversial phylogenies. While the recognition of horizontal transfer as a major factor in prokaryotic evolution

certainly complicates the interpretation of molecular phylogenies, it also allows synchronization of different parts of the universal tree of life, and thus might provide the key to the detection of periods of rapid substitutions.

Contradictions between molecular phylogenies can be either due to insufficient resolution and tree building artifacts (the placement of the microsporidia either at the root of the eucaryal domain or with the fungi probably falls into this category); unrecognized gene duplication events; or horizontal gene transfer. In general, organismal evolution is clearly visible as the majority consensus of different molecular phylogenies (e.g. ribosomal rRNAs, ATPase subunit, elongation factors, components of signal recognition particles).

One noteworthy exception from using the majority consensus as backbone for the organismal phylogeny are the Archaea. Although many characters clearly characterize the Archaea as a group which is distinct from the Bacteria, recent genome analyses confirms earlier observations that the majority of identifiable archaeal genes are very similar to their bacterial homologues. Not only are many (most?) of the genes similar to the bacterial homologues, if gene families are analyzed in more detail, the archaeal genes are found to group within the bacterial domain, and the different archaeal genes do not even cluster together. Thus the majority consensus would dissolve both the Archaea and the Bacteria into para- or polyphyletic groups. In contrast most genes involved in genome structure, transcription, translation and chemiosmotic coupling clearly set the Archaea apart from the Bacteria. In this case the backbone of our preliminary organismal phylogeny reflects those markers which are less prone to horizontal gene transfer, and explains the many genes found in the Archaea which are bacterial in character as the result of horizontal gene transfer. The fact that so many genes found in the archaeal genomes are bacterial in character raises the question of how these genes were transferred. Initially a single horizontal transfer event was considered; however, comparison of individual gene families suggests at least several smaller transfer events.

GENES AND ENZYMES OF ANAEROBIC METABOLISM IN *SHEWANELLA PUTREFACIENS*

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Shewanella putrefaciens is a gram negative bacterium in the gamma group of the Proteobacteria. It is a non-fermentative organism capable of utilizing molecular hydrogen as an energy source, and of growth on a limited number of carbon sources, including formate, pyruvate and lactate. In contrast to this limited array of energy sources, *Shewanella* utilizes an extensive array of electron acceptors for metabolism, including oxygen (aerobic respiration), N (nitrate and nitrite), Mn (Mn(III) and Mn(IV) oxides), Fe (Fe(III) oxides), S (elemental sulfur, thiosulfate, sulfite, tetrathionate, and dimethylsulfoxide), trimethylamine oxide, fumarate, glycine, and others. Given this wide range of electron potentials available, it was hypothesized that perhaps within this single organism could lie an understanding of the evolution of anaerobic respiration. We have thus been on a program of cloning, sequencing and comparing the various reductases and cytochromes used by *Shewanella* for its diverse respiratory functions. We report here the purification and properties of several different cytochromes of redox potentials ranging from -250 to +340 meV, and of several key proteins and/or genes involved in the metabolism of manganese, iron, sulfur, nitrogen, and carbon compounds.

VIABLE BACTERIA IN SIBERIAN AND ANTARCTIC PERMAFROST

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Viable bacteria were isolated from permafrost core samples from northeast Siberia. The samples were obtained from different depths, the deepest was 3 million years old. The average temperature of the permafrost was -10°C . Twenty-nine bacterial isolates were characterized by 16S rDNA sequencing. All strains grew well under anaerobic conditions. None of the strains was a true psychrophile. Phylogenetic analysis revealed that the isolates fell into four categories: high-GC Gram positive bacteria, β -proteobacteria, γ -proteobacteria and low-GC Gram positive bacteria. Most low-GC Gram positive bacteria came from 5000-8000 year old samples, and most of the other groups from 1.8 - 3.0 million year old samples.

In Antarctica, drillings were performed at three localities in the McMurdo Dry Valleys area. The oldest sample was at least 2 million, possibly 15 million year old, permafrost temperatures were -18°C , -21°C , and -25°C to -27°C . Each core contained viable bacteria, including anaerobes, their number varying up to $102\text{-}103\text{ g}^{-1}$ by plate counts and to 105 g^{-1} by fluorescence. Most samples contained methane in quantities up to 670 mL kg^{-1} of biological origin (presumably by bacteria), shown by its isotopic composition ($\delta^{13}\text{C} = 54.8\text{‰}$). Enzyme (invertase) activity was present in most samples. The ice content of all samples was unexpectedly high, at least 25% and up to 50%. Our findings revise ideas about the "dry" Antarctic permafrost.

These results provide support to the idea that martian permafrost may contain ground ice and that ancient permafrost on Mars may contain samples - possibly viable - of life forms from an earlier, wetter period.

POLAR ANALOGS TO MARS

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Mars was probably quite cold even during its presumed warm and wet period. For this reason the study of polar regions on Earth has been particularly fruitful as an analog for early Mars. The observation that fluvial features on Mars were localized, possibly restricted to regions of geothermal activity, and the difficulty of constructing self-consistent CO_2 greenhouse models for Mars imply that early Mars was quite cold and that fluvial features formed in association with a cold climate regime. Polar regions provide important analogs to an early cold Mars in two ways. First, by elucidating the physical process that allow liquid water to exist when the mean annual temperature is below freezing and, secondly, by providing examples of the biological and fossil-forming processes operating in cold climate regions. Liquid water can be maintained in permafrost by the insulating properties of an ice cover or by geothermal activity, even when temperatures are below freezing.

THE END PERMIAN MASS EXTINCTION: GEOCHRONOLOGY AND PATTERNS OF EXTINCTION

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The mass extinction at the end of the Permian was the most extensive biotic crisis in the history of life, but determining its cause has been hampered by a lack of high-precision ages. Authors have proposed several patterns: two distinct extinction peaks; a long period of increased extinction beginning in the late Middle Permian accelerating to a rapid pulse at the close of the Permian; or a very rapid extinction just at the close of the Permian and perhaps extending into the earliest Triassic. Discriminating between these extinction patterns, and between the plethora of proposed causes of the extinction, including extraterrestrial impact, massive volcanism and rapid climate change, requires high-resolution geochronologic age determinations and precise stratigraphic information on taxon occurrences. Analysis of this event provides perhaps the best opportunity to identify the impact of endogenous and exogenous events on the survivability of complex life.

Although the Permo-Triassic boundary in south China has been previously dated at 251.2 ± 3.4 Ma by SHRIMP U-Pb zircon analysis, and 250.0 ± 0.2 Ma by $^{40}\text{Ar}/^{39}\text{Ar}$ analysis, estimates of the duration of the Wordian-Changxingian stages have varied from 10 to 21 my. There are fewer estimates of the duration of the Changxingian Stage, but estimates of late Permian (Wuchaipingian plus Changxingian) durations range from 5-16 my. The numerous Permo-Triassic (P-T) marine boundary sections in South China provide critical data on the pattern of extinction, and are interbedded with abundant volcanic ash beds, which now provide the first constraints on the duration of the extinction. Uranium-lead zircon data from the Late Permian and Early Triassic rocks in South China essentially confirm (with a precision of ± 500 ky) earlier estimates of the age of the Permo-Triassic boundary. Excellent biostratigraphic control on additional ash beds indicate that the final, Changxingian Stage of the Permian lasted about 1.5 million years. Samples from west Texas just below the Wordian/Capitanian (mid-Permian) boundary indicate a duration of about 13 million years for the Capitanian through Changxingian stages.

These results confirm that the final pulse of extinction occurred in less than 1 my, coincident with pervasive geochemical changes at the close of the Permian. These ages also shed additional light on rates of paleontological and geochemical change in the latest Permian, and allow critical tests of a variety of extinction scenarios.

ORDOVICIAN BIODIVERSITY: GEOGRAPHY AND ENVIRONMENT

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The Ordovician Period was among the most dynamic intervals in the history of life. During the period, global biodiversity increased at unprecedented rates (the Ordovician Radiation), there was an apparently protracted transition in dominance among major biotic elements, and the interval culminated in a mass extinction that, on a percentage basis, may have been second in intensity only to

the Late Permian event. Despite the broad recognition of these attributes, which are readily apparent in synoptic, global diversity compilations, there is still much to learn about the ways in which they played out locally and regionally; their prominence at the global scale does not necessarily imply that these transitions took place uniformly or randomly around the world. The central goal of my ongoing research has been to investigate the possibility that this significant interval in the evolution and proliferation of life was focused geographically or environmentally in settings with unique attributes. More generally, this research addresses the extent to which the evolution and diversification of advanced life, at scales ranging from local to global, has been mediated by physical processes and events.

At the heart of this investigation is the compilation and analysis of a database that depicts occurrences of Ordovician genera in strata worldwide. Because the database also contains a variety of subsidiary data concerning the paleogeographic, paleoenvironmental, and geologic settings of each occurrence, it permits investigation of myriad questions related to the general themes of the project. Data compilation is ongoing, but the database is now sufficiently extensive to permit evaluation of several questions related to Ordovician biodiversity. To date, my primary activities have included: 1) the analysis of sampling effects on the raw, global diversity trajectory through the period, which showed that the trajectory could not be accepted at face value and indicated that most of the global diversity increase was concentrated in the first half of the period; 2) the demonstration of a geographic linkage between the Ordovician Radiation and likely regions of tectonic activity; 3) the recognition that diversification attributes differed strikingly from paleocontinent-to-paleocontinent, partly reflecting their relative proximities to tectonic activity; 4) the discovery that Ordovician genera, on average, expanded their geographic and environmental ranges significantly as they aged, which explains a surprising difference between Ordovician diversity trajectories at different hierarchical levels; 5) a preliminary confirmation of previous suggestions that the Late Ordovician mass extinction selectively eliminated taxa with limited geographic ranges, which raises the possibility that this event was also selective with respect to taxon age.

WAS HIGH OBLIQUITY THE CAUSE OF LOW-LATITUDE PRECAMBRIAN GLACIATION?

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Earth has experienced two episodes of apparent low-latitude glaciation in its history, with the first occurring in the Huronian (~2.2 Ga) and the second in the Late Proterozoic (~750-550 Ma). This suggests that either Earth was globally frozen over at those times or that Earth's obliquity was >54 degrees so that climatic zonation was reversed and the equator was the coldest part of the planet. The main objection to the so-called "snow-ball Earth" scenario is that a global ice blanket would have likely eliminated all photosynthetic life on the planet, contrary to the evidence of uninterrupted life in the fossil record. Furthermore, the high albedo of the global ice cover and overlying CO₂ and H₂O clouds may have prevented Earth from ever escaping its frozen state. To reconcile the geologic record with the past and present evidence of life on the planet, we assume that Earth's obliquity was >54° for most of its history, possibly as a result of the formation of the Moon. [The present inclination of the lunar orbit is also better explained if Earth started out at high obliquity.] The obliquity is postulated to have dropped rapidly during the last glacial period to its present value <25° by 430 Ma (in agreement with the fossil and glacial record) as a consequence of climate friction.

Climate friction is a secular change in obliquity caused by large-scale changes to the planetary ice cover and depth of oceans during an ice age. The displacement of water from the oceans to continental glaciers changes the oblateness of Earth slightly, which affects both the rate of spin-axis

precession and the regular obliquity variation. Thus, after one obliquity cycle (lasting 41 Kyr today, but 28 Kyr 600 Ma) the spin axis is displaced slightly from its original starting point, and the obliquity changes gradually over time. The rate of obliquity change depends mainly on the size of the oblateness variations. Changes to Earth's oblateness and, hence, obliquity for the most recent Quaternary ice ages are thought to have been negligible because of the small continental area underlying the glaciers. However, changes to oblateness may have been over four times as large during the Late Proterozoic when the bulk of Earth's continents are thought to have been clustered around the South Pole and the surface area affected by ice loading and unloading was maximized. The sign of the obliquity drift depends on the time lag between the obliquity/insolation oscillation and the glacial oscillation. Under the assumption of maximum glacial coverage and a short (<1000 years) glacial variation time lag, the secular change in obliquity is calculated to be $-0.2^\circ/\text{Myr}$. This would allow the obliquity to fall by as much as 30° in under 150 Myr, which would bring the obliquity from 55° down to 25° in the time available. Thus, we are enabled a self-consistent, physically plausible explanation for the low-latitude glacial climate of early Earth.

PALEOBIOLOGY OF THE TERMINAL PROTEROZOIC: PRELUDE TO THE CAMBRIAN EXPLOSION

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The Cambrian Explosion of complex life is the most obvious biological event in the history of the Earth. Much of the research aimed at understanding this milestone in the evolution of life has focused on the Cambrian fossil record, such as the famous Burgess Shale. However, many of the evolutionary innovations were underway by before the beginning of the Cambrian. This research explores those innovations in the superb terminal Proterozoic successions of Namibia, Nevada, Newfoundland and South Australia.

Recent discoveries in Nevada and Namibia have taken core members of the Ediacara "fauna" to the end of the Proterozoic, thus closing the stratigraphic gap (Kotlin interval) that had been assumed to separate the Ediacaran biota from the Cambrian explosion. The times of origin of the Ediacaran organisms and the animal phyla remain unknown but U-Pb ages on the ash bed that covered an already diverse Ediacaran assemblage at Mistaken Point, Newfoundland, are approximately 20 million years older than the base of the Cambrian. Molecular clocks indicate a significantly longer Precambrian history for the Metazoa, but the oldest metazoan trace fossils are no older than ~550 million years.

Key questions concerning the nature of the Ediacaran organisms remain unresolved but there is good morphologic and taphonomic evidence for the presence of several major clades (fronds, petalonamans, trilobozoans, etc.), that are uncomfortably united in Seilacher's extinct kingdom, the Vendobionta. Furthermore, old misconceptions are being discarded as we learn more about these enigmatic organisms from recent discoveries in Namibia, Newfoundland, Nevada, and South Australia.

Few, if any, of the Ediacaran organisms belong to the crown groups of animal phyla, none were cnidarian jellyfish, and some of the best known forms (*Dickinsonia*, *Emietta*, *Phyllozoon*, *Pteridinium*) are difficult to place in any extant animal or plant group. However, even these "core vendobionts" differ significantly from each other in the fundamental properties of construction, growth, mode of preservation, and symmetry. Together with the associated carbonate skeletons and trace fossils, the Ediacaran organisms provide a glimpse of biodiversity at the close of the Proterozoic. It is the synchronous appearance of distantly related clades of megascopic organisms that points to the poverty of intrinsic rather than extrinsic explanations for the nature of the Cambrian explosion of multicellular life.

CO₂ GREENHOUSE IN THE EARLY MARTIAN ATMOSPHERE: SO₂ INHIBITS CONDENSATION

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Many investigators of the early martian climate have suggested that a dense carbon dioxide atmosphere was present and warmed the surface above the melting point of water (*e.g.* Pollack *et al.* 1987). However, Kasting (1991) pointed out that previous thermal models of the primitive martian atmosphere had not considered the condensation of CO₂. When this effect was incorporated, Kasting found that CO₂ by itself is inadequate to warm the surface.

SO₂ absorbs strongly in the near UV region of the solar spectrum. While a small amount of SO₂ may have a negligible effect by itself on the surface temperature, it may have significantly warmed the middle atmosphere of early Mars, much as ozone warms the terrestrial stratosphere today. If this region is kept warm enough to inhibit the condensation of CO₂, then CO₂ remains a viable greenhouse gas. Our preliminary radiative modeling shows that the addition of 0.1 ppm of SO₂ in a 2 bar CO₂ atmosphere raises the temperature of the middle atmosphere by approximately 10 degrees, so that the upper atmosphere in a 1D model remains above the condensation temperature of CO₂. In addition, this amount of SO₂ in the atmosphere provides an effective UV shield for an hypothetical biosphere on the martian surface.

DIFFUSION OF PHOTOCHEMICALLY PRODUCED HYDROGEN PEROXIDE IN THE MARTIAN REGOLITH

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The initial biological examination of Mars by Viking failed to detect life; instead the Viking experiments revealed that regolith material apparently contains chemical oxidants and is devoid of organic material at the surface (*e.g.*, Klein, 1979). Since reducing materials that are relict of prebiotic chemical evolution are susceptible to chemical attack by such oxidants, their recovery is contingent upon penetrating oxidized strata. Zent and McKay (1994) concluded that the most consistent explanation for the Viking results calls on photochemically produced oxidants (odd-hydrogen and odd-oxygen species), which originate in the atmosphere and diffuse into the regolith. One study of the diffusion of hydrogen peroxide into the regolith (Bullock, *et al.* 1993) has suggested that the depth of the oxidized layer may be no more than several meters, although that modeling study was limited by the lack of data on the lifetime of hydrogen peroxide against reaction in the regolith, and its adsorptive behavior.

We report on experimentally determined rate constants and activation energies for the catalytic destruction of hydrogen peroxide vapor by martian soil analogs. From these rate constants the lifetime of hydrogen peroxide at Mars-like temperatures is calculated for each analog material. Fitting this new data into the model of Bullock *et al.* (1993) yields estimates of the penetration depth of hydrogen peroxide in the martian regolith. We find that for a basaltic analog material where the predominate iron phases are ferrous the lifetime of hydrogen peroxide at 215° K is on the order of 105 seconds, which corresponds to a penetration depth of 7 mm into the martian regolith. From the Viking GC-MS data we know that the minimum depth of oxidized strata at the landing sites is approximately 10 cm. Therefore,

for a soil with an abundance of ferrous iron minerals, models of regolith mixing by wind or impact cratering must be invoked if hydrogen peroxide is the oxidant responsible for the decomposition of organic material. In the case of analog materials where the predominate iron phases are ferric, the lifetime of peroxide is greater, however, regolith mixing, not diffusion, may still be the dominate mechanism of oxidant transport in the martian regolith.

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THE SUDBURY IMPACT EVENT: EFFECTS ON CARBONACEOUS MATTER

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The large (~200 km dia.), ancient (1.85 Gya) Sudbury Impact Crater contains exceptionally high amounts of C in the Onaping Fm impact deposits (avg. 0.6 wt %) and in the overlying post impact, water lain deposits of the Onwatin Fm (avg. 2.8%). Our primary objectives are: characterize carbonaceous components and their distributions, identify their potential sources, contribute to modeling P, T, t conditions in the impact plume and establish when life reappeared in the region.

Fullerenes (C₆₀ and C₇₀) have been found in the Onaping Fm /1/ and are attributed to impact formation, although a small number of these fullerenes contain trapped He with ³He/⁴He ratios of interstellar signature /2/ which implies extraterrestrial origin of some fullerenes and impact survival. We have since found fullerenes of C numbers C₇₄, C₇₈, C₈₄ and C₁₀₀; the significance of these less stable fullerenes is presently unclear. Raman spectroscopy shows that the bulk of the C is highly disordered graphite (impact processed). Amino acids are terrestrial in origin and recent (<200 Kya). Low concentrations of PAHs were found only in the Onwatin sediments. Soot (formed only by combustion) has been found in a sample from the lower Onwatin. Our preliminary bulk δ¹³C data together with published bulk analyses /3,4/ show a trend from very light carbon (-39 ‰) in the melt zone, through the Onaping (-32 to -27‰) to heavier carbon in the lower Onwatin (-25 to -21‰). Although the Onaping data are consistent with biological activity, little supporting evidence has been found. We suggest that the trend is the result of impact processing of carbonaceous matter (mostly kerogen; avg. -29‰) that was present in the surface rocks before impact. In addition, contributions may have come from the impactor and dissociation of C from carbonate by impact evaporation. In contrast, the heavier C in the Onwatin sediments could be the result of sulfate reducing bacteria /4/. Small carbonate platforms in the C-rich mudstones (slates) of the lower Onwatin may have formed via hydrothermal venting from the deeply buried, hot impact zone. Some evidence of algal activity is also present.

Soot (formed from the combustion of C during impact) may constrain the time of Onaping deposition and the appearance of life (bacteria/algae) in that the fallout time of soot from the stratosphere is <2 years. If this is correct, then the Onaping formed within 2 years and fresh water or marine deposition commenced together with possible incipient sulfate reduction, anoxygenic photosynthesis and methanogenesis.

In contrast to being an entirely destructive event to life, the impact may have actually helped to rapidly reestablish life in the region by furnishing nutrients and favorable environments.

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METEORITE IMPACT PRODUCTION OF VOLATILES AND THEIR BIOSPHERIC EFFECTS AT THE CRETACEOUS/TERTIARY BOUNDARY

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Impact cratering played a dominant role in the evolution of the terrestrial planets prior to 3.8 billion years (Ga) ago. Life may have first appeared on Earth near the end of this heavy bombardment period, but most evolution occurred since, during a period when large impacts were rare. Impacts were largely ignored in the evolution of the Earth's biosphere until the discovery of meteoritic debris at the Cretaceous/Tertiary (K/T) boundary (65 million years ago), which led to the proposal that a large impact caused the mass extinction of life that marks this geological boundary. Analyses of global, synoptic paleontological databases covering the last 500 million years have identified five such extinctions events when a large percentage of Earth's species went extinct over a very brief period of time. These crises mark major shifts in evolutionary trends and play a critical role in the evolutionary process. Large impacts have been correlated with other extinction events and we now recognize that large impacts played a major role in the evolution of life on Earth and perhaps on Mars.

The discovery that the Chicxulub crater in Mexico is the site of the K/T impact helped focus research on the importance of target lithology, which at Chicxulub consisted of large amounts of water, carbonate, and sulfate. Our comprehensive analysis of these target volatiles strongly supports the hypothesis that impact-generated sulfate aerosols caused over a decade of global cooling, acid rain, and disruption of ocean circulation, which contributed to the mass extinction at the K/T boundary. The crater size, meteoritic content of the K/T boundary clay, and impact models indicate that the Chicxulub crater was formed by a short period comet or an asteroid impact that released 10³¹ ergs of energy. Impact models and experiments combined with estimates of volatiles in the projectile and target rocks predict that over 200 gigatons (Gt) each of SO₂ and water vapor, and over 500 Gt of CO₂, were globally distributed in the stratosphere by the impact. Modeling of the aerosol clouds demonstrates that: 1) if the initial rapid pulse of sulfate aerosols was global, photosynthesis may have been shut down for 6 months, and 2) that a second prolonged aerosol cloud, reduced solar transmission 80% by the end of first year and remained 50% below normal for 9 years. As a result, global average surface temperatures probably dropped between 5° and 31° K, suggesting that global near-freezing conditions may have been reached. Impact-generated CO₂ caused less than 1° K greenhouse

warming and therefore was insignificant compared to the sulfate cooling. The magnitude of sulfate cooling depends largely upon the rate of ocean mixing as surface waters cool, sink, and are replaced by upwelling of deep ocean water. This upwelling apparently drastically altered ocean stratification and circulation, greatly prolonging the impact effects.

SHOCK SYNTHESIS OF ORGANICS IN COMETARY IMPACTS

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Recent paleontological evidence indicates that life was present on Earth as early as 3.9 Gyr ago. In this case life arose on this planet during the late stages of accretion. It is likely that the main influx of volatile material during this time was due to cometary infall. We use the known composition of Comet Halley to model the probable composition of an atmosphere dominated by cometary volatiles. We also present experimental results which show that shock processes in an atmosphere of cometary volatiles are capable of producing organic compounds that could have been relevant to the emergence of life.

DEVELOPMENT OF A LASER RAMAN SPECTROMETER FOR *IN SITU* EXOBIOLOGY EXPLORATION

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This is the third progress report, following those presented at the Conference on Early Mars (April 24-27, 1997), and at the Laser Raman Workshop (June 6, 1997) and the PIDDP Meeting (June 10-11, 1997). Activities taking place since the last report include: a) demonstration of in situ wavelength calibration of the spectrometer using Fraunhofer lines of the solar spectrum obtained from atmospheric scattered sunlight; b) demonstration of the transmission of a laser Raman signal through a polyimide coated optical fiber subjected to temperatures as low as 141° K (-132° C); and c) determination of the spectral sensitivity of the Raman probe, fiber link, and spectrometer as a system using a standard lamp. The first two items of course are important if a laser Raman spectrometer is to be used on Mars, and the last item permits presentation of spectra on a normalized scale. Now that a sensitivity calibration has been obtained, we have begun software development for extraction of weak signals from "dark" samples and Raman peaks that are superimposed upon strong photoluminescence or Rayleigh scattering backgrounds.

The work has utilized our Mark Ia device, which incorporated a room temperature CCD detector (the Mark I version employed a diode array) and a "large" diode laser, which, along with a miniaturized Raman probe, serves as a test bed. A new spectrometer incorporating a cooled CCD detector array and packaged smaller than the "video cassette size" Mark Ia/I system is under construction by our industrial partner under a shared costs program. Also importantly, we have engaged with another industrial partner to develop a 20 mW diode laser, suitable for Raman spectroscopy, that is in a package having dimensions of 8.9 cm x 8.9 cm x 2.5 cm (the footprint of a 3.5 inch computer disk, but 1 inch thick). The combined Mark II laser Raman system, spectrometer, laser, and Raman probe components are of a size (fit in a single hand) and mass suitable for deployment on spacecraft contemplated for the beginning years of the next millennium (Mars Surveyor 2001 and beyond).

Finally, we are continuing our program to obtain laser Raman spectral signatures of interest to planetary exploration and specifically exobiology. In September, 1997, samples of the Onaping carbonaceous member of the Sudbury impact structure were obtained for use as analogs for what might be associated with impact craters in the martian Highlands. Our laser Raman spectrometer project has moved into the new 1000 square ft. Laboratory for Instrumentation for Space Exploration (LISE).

NON-ENZYMATIC OLIGOMERIZATION OF MONONUCLEOTIDES USING NON-STANDARD OLIGONUCLEOTIDE TEMPLATES

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The origin of life on the Earth is likely to have begun with self-replicating polymers. Of all extant natural molecules, RNA comes closest to exhibiting the requisite properties of the first self-replicating polymer. The main reason for this consideration is its capability of serving both genotypic and phenotypic roles. However, RNA is an imperfect candidate for the first genetic material in several respects. The work to be presented focuses on the possibility of replication within four alternative genetic systems: i) 2',5'-phosphodiester linked nucleic acids, ii) glycerol-nucleic acids, iii) iso-cytosine and iso-guanine based nucleic acids, and iv) universal triplex forming nucleic acids. Results in all four areas will be discussed, including the recent finding that 2',5'-linked RNA is a competent template for the non-enzymatic synthesis of RNA.

TEMPLATE-DIRECTED SYNTHESIS OF DNA-PNA CHIMERAS

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It is widely believed that the familiar RNA/DNA/protein world was preceded by an RNA world, that is a world from which coded proteins were absent. However, the de novo origin of the RNA world is problematical, since there are major obstacles to the prebiotic synthesis of nucleotides. Several authors have proposed, therefore, that the RNA world was preceded by some other world controlled by a genetic system simpler than RNA. This raises acutely the problem of information-conserving transitions between genetic systems. Here we study one relevant pair of reciprocal transitions, from peptide nucleic acids (PNAs) to nucleic acids and vice versa.

In earlier experiments we have shown that PNA templates will direct the synthesis of complementary RNA products and vice versa. We have now completed a study of chimera formation, that is the ligation of DNA and PNA on either a PNA or a DNA template. We find that chimera-function via a phosphoramidate bond is efficient when the ligation junction is isostructural with a DNA backbone, but not otherwise. Ligation via a 3'-phosphoramidate bond is particularly rapid and efficient. Ligation via a 3'-phosphoramidate bond is less efficient, owing to the low nucleophilicity of the 5'-OH group of DNA. Replacement of the 5'-OH group by a 5'-NH₂ group gives a substrate which ligates efficiently via a 5'-amide bond.

TITAN HAZE: CYANOACETYLENE AND CYANOACETYLENE-ACETYLENE PHOTOPOLYMERS

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The solar UV photolysis of the gases present in the atmosphere of Titan is believed to be the source of the organic haze which obscures the view of Titan's surface. The photochemical processes leading to this haze provide a model for how complex molecules may have formed from simple ones in the atmosphere of the primitive Earth. We have undertaken a study of the photolysis of cyanoacetylene and cyanoacetylene-acetylene mixtures since these are two of the atmospheric compounds which absorb solar UV strongly on Titan. Structural analysis of these polymers may contribute to our understanding of the data returned from the Huygens probe of the Cassini mission that will pass through the atmosphere of Titan.

Mechanistic studies established that the photodissociation of cyanoacetylene to a hydrogen atom and the cyanoethyl radical proceeds with a quantum yield of 0.09. Previous studies established that the photodissociation of cyanoacetylene into cyano- and ethynyl- radicals has a quantum yield of 0.05 so the formation of the excited state of cyanoacetylene must proceed with a quantum yield of 0.86. Free radical addition and abstraction processes predominate in the subsequent reactions following the photodissociation of cyanoacetylene present in the atmosphere of Titan.

Photolysis of acetylene in the presence of cyanoacetylene results in the polymerization of both monomers. Quantum yield measurements established that cyanoacetylene is 2-5 times as reactive as acetylene for polymer formation. The structure and morphological properties of polymers produced photochemically from the UV irradiation of cyanoacetylene and cyanoacetylene mixtures have been examined in order to evaluate their possible contribution to the haze layers found on Titan. Infrared analysis, elemental analysis and thermal methods (thermogravimetric analysis, thermolysis, pyrolysis) were used to examine structure of polycyanoacetylenes produced by irradiation of gas phase HC_3N at 185 and 254 nm by itself and in the presence of Titan's other atmospheric constituents (CH_4 , C_2H_6 , C_2H_2 and CO). Of special significance is the copolymer of HC_3N and acetylene. Even though acetylene was absorbing nearly all of the incident photons, the ratio of acetylene to HC_3N found in the resulting polymer was 2:1. Scanning electron microscopy (SEM) was used to visually examine the polymer particles.

ABIOTIC ORGANIC SYNTHESIS UNDER SIMULATED HYDROTHERMAL CONDITIONS

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Ever since their discovery in the late 1970s, mid-ocean-ridge hydrothermal systems have received a great deal of attention as a possible site for the origin of life on Earth (and for potential origins of life on Mars and elsewhere as well). Because no modern-day terrestrial hydrothermal systems are free from the influence of organic compounds derived from biologic processes, confirmation of the potential for organic synthesis in hydrothermal systems must come from laboratory experiments. Assessing the potential for organic synthesis in prebiotic hydrothermal systems requires a better understanding of

reaction pathways and effects of the chemical and physical variables of the environment by carrying out additional laboratory simulation experiments.

We report on research projects directed toward addressing these issues. Presently, our research focuses on several areas: 1) understanding the factors (kinetic vs. thermodynamic) that control reactions involving organic compounds in hydrothermal systems, 2) the formation of lipid compounds during Fischer-Tropsch-type synthesis in an aqueous environment from formic or oxalic acids, 3) the formation of organic compounds from decomposition of iron oxalate, and 4) the synthesis of amino acids during the serpentinization of olivine. The hydrothermal Fischer-Tropsch-type synthesis has been most successful, producing lipid compounds ranging from C₂ to >C₃₅ and consisting of n-alkanes, alkenes, n-alkanoic acids, n-alkanols and alkanones. The precursor carbon sources were formic acid, which disproportionates to H₂, CO₂, and CO, and oxalic acid, which disproportionates to H₂ and CO₂. Both yield essentially the same range of compounds.

HYDROTHERMAL ECOSYSTEMS IN A PLANETARY CONTEXT

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Diverse lines of evidence converge on the hypothesis that life emerged on the Earth in water at elevated temperatures like those encountered in hot springs and hydrothermal systems. The phylogenetic tree constructed from small subunits of RNA indicates that the hyperthermophiles populate the lowest branches. By inference, these organisms are closest (in an evolutionary sense) to the common ancestor of the three domains of life. This fact has been used to argue that the common ancestor was also a hyperthermophile. This does not demand that high temperatures were required for the emergence of the first living system, and researchers have argued that organisms in sea floor hydrothermal systems may have been the only survivors of the last large impact during late-stage accretion. However, the conditions of submarine hydrothermal systems are uniquely suited to the synthesis and preservation of organic compounds. It follows that hydrothermal systems may be similarly conducive to the emergence of living systems. As a consequence, hydrothermal systems are often put forth as likely ecosystems throughout the solar system.

Our goal is to develop models to test whether likely geophysical, petrologic and geochemical processes during the formation and early evolution of Earth, Mars, and Europa could have produced hydrothermal systems capable of supporting life. The criteria adopted to indicate whether a system is capable of supporting life include: 1) disequilibrium states derived from water/rock reactions and fluid mixing that favor the synthesis of organic compounds from CO₂, CO, or nebular condensates, and 2) additional redox disequilibria involving iron and sulfur minerals, and iron, sulfur and nitrogen aqueous species that possess sufficient energy to drive metabolic processes. Our guide to likely sources of chemical energy is provided by the overall metabolic processes of the deepest-branching organisms of the terrestrial phylogenetic tree. These hyperthermophilic microbes pursue lithoautotrophic lifestyles that are independent of light energy. Instead, consortia of microbes take advantage of geologically-provided geochemical disequilibria. As a consequence, they provide models of plausible subsurface ecosystems for other planets with liquid water and sources of heat. However, there is considerably more to hydrothermal habitats than hot water and carbon. Fluid and rock compositions have to be able to provide enough energy to drive metabolic processes, and geophysical and petrologic processes have to be able to generate those fluid and rock compositions.

Outside of the Earth and Mars, the jovian moon Europa is emerging as a prime site of exobiological interest, especially as evidence for an ocean underneath its icy surface continues to accumulate.

Measurements of Europa's gravitational moments strongly suggest that Europa has differentiated into a structure not unlike that of the Earth: an iron core, rock mantle, and thick (~150 km) surface water/ice layer. Hydrothermal systems are an inescapable consequence of volcanic activity in the presence of liquid water, and would have been abundant during heating, differentiation and cooling phases of Europa's evolution. After differentiation, rock compositions are likely to be basaltic in the parts of the rock mantle that would be in close proximity to the ice layer. If so, hydrothermal systems would have been hosted in basalt for the past ~3.5 b.y., including systems that might accompany present-day rock-mantle/ice-layer boundary volcanism. Preliminary calculations reveal that such systems have a high potential for synthesis of organic compounds from inorganic nitrogen and carbon compounds likely to be in Europa's ice (and ocean).

**ANOXIA AND EVOLUTIONARY PATTERNS IN THE SEA:
ONSHORE/OFFSHORE TRENDS AND RECENT RECRUITMENT
OF THE DEEP-SEA AND HYDROTHERMAL VENT FAUNAS**

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The role of oxygen concentration as a controlling factor on the evolution of eukaryotes and macrofauna has been a recurring theme in studies of Earth's Precambrian biota. More recently the role of ocean-wide anoxic episodes in generating Phanerozoic extinction events, such as the Permo-Triassic has received considerable attention. We argue that oxygen concentration has played a more pervasive role in shaping the pattern of macro-evolution in Phanerozoic oceans. Over the last 15 years a striking pattern has been documented in the fossil record of benthic invertebrates. Higher taxa (orders) tend to originate onshore, diversify offshore, and retreat into deep water environments. Previous studies attribute this macro-evolutionary pattern to the role of disturbance in mediating biotic interactions in the near shore environment, which in turn permitted evolution of novel forms accorded ordinal rank. However, this onshore/offshore pattern of ordinal origination is not uniform over geologic time. In the Post-Paleozoic, onshore origination of orders occurs preferentially in the early Mesozoic, declines in the Late Cretaceous, and by the Tertiary bias in ordinal origination favors the offshore. We argue that this temporal distribution results from changes in the frequency of anoxic/dysoxic conditions in the offshore environment. Mesozoic marine rocks record anoxic/dysoxic events of global and regional scale. These reduced oxygen conditions expand outwards from graben or other basinal settings. Thus Mesozoic anoxia/dysoxia preferentially affects offshore settings. Many lower Mesozoic offshore sections contain periodic dark (anoxia related) shales suggestive of Milankovitch climatic forcing. Sediments indicative of low oxygen conditions are much less pervasive in the Tertiary. This decline is consistent with the shift from a "greenhouse" world with warm polar regions and limited thermal circulation of the deep ocean, to an "ice-house" world with more dynamic delivery of oxygen to the deep ocean. Loss of an anoxia/dysoxia-related fauna, as well as an increase in burrowing, document a biological response to more pervasively oxygenated conditions beginning in the Late Cretaceous.

Pervasive anoxia has additional implications for the evolution of the deep-sea fauna. Major events such as that at the Cenomanian/Turonian boundary, must have disrupted much, if not all, of the deep sea habitat for normal marine as well as vent related benthose. Thus the deep sea can not have been continuously and widely inhabited without disruption. The deep sea faunas must have experienced a biogeographically complex history in the Mesozoic involving retreat to more appropriately oxygenated regions, most likely in shallow water. Vent organisms of all stripes also require oxygen. Even

chemosynthetic bacteria require redox gradients. Thus theories of the vent origin of life must also accommodate the changing topology of interaction between redox gradients in the sea and hydrothermal activity.

MÖSSBAUER SIGNATURES THAT MAY BE USEFUL IN IDENTIFYING RESIDUES OF ANCIENT MARTIAN HYDROTHERMAL SYSTEMS

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Iron-rich thermal springs may have been present on early Mars and served as environments suitable for possible ancient martian life. The residues left by such structures, if they existed in the past, would be amenable to spectroscopic investigation. A Mössbauer spectrometer, which focuses on iron-containing materials, is likely to be employed as an in situ instrument during a future mission to Mars. Therefore, we have been investigating the nature of information Mössbauer spectroscopy can provide about such hydrothermal deposits and whether spectral signatures exist that would be characteristic of them or of any biomarkers they might contain.

Among our first results in this effort was the identification of nanophase iron oxides in hydrothermal deposits collected at Manitou Springs, CO, and at Chocolate Pots, Yellowstone National Park. Such fine-grained material is a characteristic of subaerial hydrothermal sediments and would serve as a potential fossilizing medium. Recently, we have investigated a suite of samples collected from several locations, and at several depths up to ~1 cm, along the outflow channel of a large vent mound at Chocolate Pots.

Most samples show the spectral signatures of siderite, $\text{Fe}^{2+}\text{CO}_3$, and nontronite, $(\text{CaNa})_{0.66}\text{Fe}^{3+}_4\text{Si}_{7.34}\text{Al}_{0.66}\text{O}_{20}(\text{OH})_4n\text{H}_2\text{O}$, a member of the smectite group of clays. Goethite, FeOOH , and hematite, Fe_2O_3 , have also been observed. The presence of siderite and nontronite in all samples (except those very near the vent or the surface, which are amorphous) has been confirmed by XRD and is consistent with major element analysis.

A localized deposit of nanophase material on Mars would suggest an ancient hydrothermal spring. To identify such material, the acquisition of Mössbauer spectra at different temperatures (diurnal variation) would likely be necessary. On the other hand, an association of siderite and nontronite, for example in the interior of a martian rock, could be identified by Mössbauer spectroscopy with a single measurement. Such a finding would be consistent with a hydrothermal origin and thus suggest a site of potential exobiological interest. The presence of all three signatures would be even more definitive.

EXPLORATION OF MONO LAKE USING TROV: APPLICATION OF TELEPRESENCE TECHNOLOGY TO EXOBIOLOGY STUDIES

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The search for a fossil record of life on Mars is a key goal of the Mars Surveyor program. Two key environments where life on Mars may have occurred include hypersaline lakes and hydrothermal springs. The study of modern analogs of these environments provides important information leading to an understanding of the martian environment and helps develop the context for searching for a fossil record.

This paper describes a field experiment to explore Mono Lake using the Telepresence Controlled Remotely Operated Vehicle (TROV). The goal of the experiment was to study mineralization processes associated with thermal and non-thermal spring inflow into Mono Lake, a hypersaline, alkaline lake in eastern California located in a volcanically active area. The high pH and high salinity make the lake a very hostile environment for diving. Tufa towers, large spires formed by the precipitation of calcium carbonate around cold springs on the lake floor, protrude above lake level along the lake's western shore. In addition, non-mineralizing thermal springs observed along the eastern shore of Paoha Island were traced into shallow offshore areas using the TROV. Objectives included obtaining video records of the study area, sampling water column properties, obtaining and analyzing water samples, and obtaining sediments and mineral precipitates (primarily carbonates) associated with sub-aqueous spring outflows on the floor of the Lake.

The instrument complement on TROV included: a matched pair of stereo video cameras on a rapid pan and tilt platform, a single fixed downward pointing camera. Additional capabilities included high resolution 750 KHz pencil beam sonar imaging and 1 MHz scanning sonar, instruments for measuring water column properties (C,T,D, pH), a water sampling system which pulled water into syringes, and a three function manipulator arm used to collect mineral samples and place them in a rock box carried by the TROV. TROV was navigated using a Dive Tracker acoustic navigation system. All data were continuously recorded throughout the experiment. TROV was deployed from the deck of a boat anchored above the field site. Control and data recording equipment was located on the boat. The location of the boat was continuously recorded using a differential GPS system.

Results of the experiment along with implications for applying these techniques to the study of subaqueous hydrothermal systems will be discussed.

RECOGNIZING BIOGENIC SIGNATURES NEAR LIFE'S UPPER TEMPERATURE LIMIT: THE ROLE OF HYPERTHERMOPHILIC BIOFILMS IN SPICULAR GEYSERITE MORPHOGENESIS

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Hydrothermal systems were likely to have been widespread on early Mars at a time when life had already established itself on Earth. Molecular phylogenetic studies of extant life suggest that the earliest ecosystems on our planet were inhabited by hyperthermophiles, microorganisms that define life's upper temperature limit. Whether life originated in such ecosystems or whether

hyperthermophiles were the only microbes to survive the early bombardment period remains debatable. In any case, the potential for life to exist above 113° C requires a re-evaluation of the contributions of hyperthermophiles to the formation of hydrothermal mineral deposits.

To maximize NASA's ability to recognize and assess hyperthermophilic biogenic signatures (i.e. stromatolites, microfossils, chemofossils) in the rock record, we are investigating how these signatures are preserved in modern ecosystems. Our current efforts have focused on characterizing the biodiversity of extant hyperthermophilic communities in near-boiling subaerial thermal springs, and on identifying how hyperthermophiles influence the structuring of the mineral deposits that precipitate in their presence. This work will provide a framework within which the biogenicity of ancient analogue deposits can be assessed, and will serve as a basis for evaluating the biogenicity of siliceous epithermal (shallow subsurface) hydrothermal deposits, a potentially important paleobiological repository that has yet to be characterized systematically.

We have found that the presence of hyperthermophilic biofilms influences the microstructural development of high-temperature siliceous geysers. Geysers had previously been considered abiogenic structures. We have also found that the heterogeneous distribution of biogenic laminations controls the morphogenesis of larger scale structures, such as laminated conical-shaped spicules, that are recognizable in fossilized material. Our findings demonstrate the potential for macro-scale features of ancient siliceous hydrothermal deposits that formed near life's upper temperature limit to record some aspects of the history of hyperthermophiles. Molecular phylogenetic analysis of these geysers has revealed that subaerial and subaqueous microenvironments of a spring host distinct communities that can be correlated with different geysers morphotypes. In addition, a unique, novel lineage of Bacteria was identified in subaqueous geysers sediments by C. Blank. The branch point of this organism lies closer to the root of the phylogenetic 'universal tree of life' than any other divergence identified to date. Further study of such organisms will elucidate the nature of early life on Earth, and improve our understanding of how early life diverged into the three super-kingdoms Archaea, Bacteria, and Eucarya.

FOSSILIZATION PROCESSES IN THERMAL SPRINGS: COMPARATIVE STUDIES OF MODERN AND ANCIENT SILICEOUS SPRING SYSTEMS

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Present evidence for the origin of life suggests that it developed quickly, sometime between 3.8 and 4.4 Ga. The higher heat flow, widespread volcanism, and likelihood of giant impacts during the early Archean supports the view that hydrothermal systems were probably widespread over the Earth during the time the biosphere emerged. In addition, RNA-based molecular phylogenies suggest that the last common ancestor of life was an extreme thermophile. Because hydrothermal environments have been shown to be thermodynamically favorable places for the synthesis of prebiotic organic chemicals, we must entertain the possibility that many of the earliest organisms not only lived at higher temperatures, but that life may have actually originated there.

From a paleontological standpoint, hydrothermal systems are important targets for studies of early biosphere evolution because they are usually rapidly mineralizing environments where many microorganisms are entombed by precipitating minerals and fossilized. Around vents and along spring outflows, microbiological information is captured within deposits in a variety of ways, including cellular fossils, biofabrics and biosedimentary structures (e.g. stromatolites). The rapid changes in temperature and pH observed along thermal spring outflows, and the corresponding changes in the microbiotas occupying these environments, make thermal springs excellent natural laboratories for

studying the processes of stromatolite morphogenesis and microbial fossilization over a broad range of conditions.

Petrographic thin section studies of Yellowstone sinters indicate that organically preserved microfossils are rare, being restricted to lower temperature microfacies. For the cyanobacterial mat systems of siliceous springs, the dominant mode of preservation is by surface encrustation of individual cells and filaments, followed by the rapid degradation of organic materials to produce external molds. Although rare, cyanobacterial sheaths are occasionally preserved by permineralization at temperatures below ~35° C. This indicates that even though organic matter is rapidly entombed by precipitating minerals, at higher temperatures it is quickly destroyed prior to the in-filling (cementation) of typically porous sinter frameworks during early diagenesis. In fact, the only organic materials observed in thin sections of higher temperature microfacies are plant fragments (lignin).

Comparative studies of Devonian-aged (350 Ma) sinters from the Drummond Basin (NE Queensland, Australia) revealed trends in preservation that are consistent with observations of modern thermal spring systems in Yellowstone. Oxygen isotope data obtained from the Drummond sinters over the entire paleotemperature shows a "shot-gun" pattern, indicating that primary temperature signatures were not preserved during diagenesis. The Drummond sinters also show very low total organic carbon abundances, consistent with our thin section observations of Yellowstone sinters. As with the modern sinters, the most commonly preserved organic materials in the Drummond sinters were fragments of multicellular plants. These materials tend to be more abundant at the lower temperature end of the system where higher plants are more abundant. This accounts for the slight rise in TOC values observed for low temperature microfacies. Furthermore, the carbon isotope values for the Drummond sinters show little variation over the entire paleotemperature range. The average value (-26 per mil) is what would be expected from plant materials, again consistent with the thin section observations noted above.

**THE IKIRYU SINTER
(500,000-300,000 YRS.), KYUSHU, JAPAN**

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Siliceous deposits, including hot-spring sinter and subaqueous sedimentary rocks, contain much of the early terrestrial record of life and are likely to be targets in the exploration for life on Mars. The goal of the present project is to develop criteria for distinguishing between biological and abiological features in modern and ancient siliceous hot-spring deposits that will aid in recognizing biological remains and the influence of organisms on similar deposits in the early terrestrial geologic record and on Mars.

The Ikiryu sinter is a siliceous hot-spring deposit near Kuju Volcano, central Kyushu, Japan. It crops out discontinuously for about 800 meters between an underlying 500,000-year-old rhyolitic sequence and an overlying 300,000-year-old andesitic breccia and includes two members: (1) a lower colored member up to 5 m thick composed of dense, recrystallized, largely structureless chert containing an abundance of iron and other impurities; and (2) an upper member, 4.0 to 4.5 m thick, that consists of white siliceous sinter showing well preserved primary features. These include layers of conical stromatolites and silicified filaments representing the filamentous cyanobacterium Phormidium deposited in quiescent pools at temperatures of 30-60° C.; layers of silicified horizontal streamers and

silicified flat sheet-like mats with underlying cavities, representing trapped oxygen bubbles, deposited by the bacteria *Phormidium* and *Mastigocladus* in rapidly flowing water at 30-60° C.; and layers of vertical silicified bacterial filaments representing the filamentous cyanobacterium *Calothrix* deposited in terraced pools below 30° C. No actual preserved primary organic matter, including bacterial filaments, have yet been recognized. No sinter facies were identified representing water temperatures above 60° C, although in modern systems the temperature range from 60-73° C is seldom represented by significant silica deposits. The succession of layers suggests that initial high-temperature (>30° C) outflow reaching the area represented by the present outcrops was followed by gradual cooling and sinter deposition at temperatures below 30° C. Lateral temperature relationships provide a means of locating the vent, which appears to have been removed by erosion.

The contrasts between the lower, dense, poorly-structured and upper, porous, well-structured sinter members reflect the cessation of hydrothermal activity and burial of the upper sinter member before it could be completely recrystallized and cemented by its own hydrothermal waters.

PRESERVATION OF HALOARCHAEA AND THEIR MACROMOLECULAR CONSTITUENTS IN BRINE INCLUSIONS FROM BEDDED SALT DEPOSITS

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Although results from the Viking mission appear to preclude the presence of life forms on the surface of modern Mars, the presence of life on a wetter and warmer, early Mars, cannot be precluded. The culturing of viable microorganisms (*Bacillus*) from insects trapped in 40 m.y. old amber suggests that some microorganisms have an extreme capacity for surviving geological time periods in isolation and in a physiologically inactive state. Reports of haloarchaea cultured from salt deposits as old as 200 m.y. have been attributed to the preservation of organisms entombed in brine inclusions within salt crystals. Direct proof of this, however, is lacking. Hypersaline lakes may have existed on early Mars. If so, evaporite minerals containing frozen brine inclusions may occur on the surface or near subsurface of Mars today. Direct evidence for the long term preservation of viable bacteria or DNA within brine inclusions will have an immediate impact upon the search for life on Mars, the evolution of life on Earth and on the procedures for analyzing samples from future Mars sample return missions. The overall goal of this research is to establish the survival potential of haloarchaea or their DNA in brine inclusions by analyzing bedded halite samples that vary in geological age.

Recently-deposited salt from Laguna Grande de la Sal in New Mexico was collected in order to assess and develop methods of analysis. These samples contained viable haloarchaea. PCR amplification of DNA extracted directly from four-year-old (modern) Laguna Grande de la Sal salt revealed the presence of archaea 16S rDNA. Cloned genes were sequenced, phylogenetically analyzed, and determined to be closely related to members of the genus, *Haloferax*, within the haloarchaea. In contrast, no halophilic archaea were cultured from 200 m.y. polyhalite from the Salado Formation in New Mexico. In addition, archaea 16S rDNA was not detected by PCR amplification of salt extracts. These results could be interpreted as consistent with theoretical expectations on the survival of bacteria trapped in brine inclusions. The results do not, however, provide an accurate assessment of the survival time for haloarchaea or how their macromolecular constituents survive in liquid, brine inclusions.

The focus of the current research is to investigate the potential for preservation of haloarchaea trapped within brine inclusions. A combination of microbiological, molecular, and geochemical approaches are being used to establish the chronological age at which inclusions formed and the presence of viable (culturable) halophiles and/or intact macromolecules. For this research, we have selected a sequence of bedded salt deposits in Death Valley, California which range in age from 0 to 200 kyr.

**EXPOSURE OF OSMOPHILIC MICROBES
TO THE SPACE ENVIRONMENT ON BIOPAN:
UV-RADIATION, THE EFFECT OF ANHYDROBIOSIS
AND PROTECTION MECHANISMS**

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The environment in which an organism lives plays a critical role in its evolution. This study provides a better understanding of how organisms may have developed survival strategies to protect them from a significant detrimental environmental parameter, that is, the UV-radiation flux at the early Earth's surface during life's origin and early evolution (e.g., evolving UV absorbing pigments, or adapting to life in a protective salt crystal, which involves understanding the physiology of halophily and osmophily). It is even more relevant to the potential for the evolution of life on early Mars which also had a high UV flux during its early history when life would have arose; the relevance continues to when Mars became cold and desiccated leaving organisms that could survive in evaporites as a possible last vestige for life. This last statement becomes more important in the realization that salts in the form of duricrusts may be abundant on Mars. By extension this also has relevance to Mars Exobiology site selection in the search for evidence of a possible past martian biota if evaporitic material served as the last vestige for a possible martian biota. Lastly, This research provides new data useful for the technical and programmatic decisions that must be made regarding planetary protection requirements for future missions, especially those to Mars.

The objective of this study is to determine the survivability of osmophilic microorganisms in space, as well as examine the DNA breakage in osmophilic cells exposed to solar UV-radiation plus vacuum and to vacuum only. The BIOPAN facility is used to accomplish the objective of the study. BIOPAN (a pan shaped biological facility developed to fly in Earth orbit on recoverable satellites) was developed by the European Space Agency (ESA) to conduct experiments leading to a better understanding of the responses of microbes to space vacuum and solar UV-radiation. The organisms used in this study were an unidentified species of *Synechococcus* (Nägeli) that inhabits the evaporitic gypsum-halite crusts that form along the marine inter-tidal, and an unidentified species of the extremely halophilic genus *Haloarcula* (designated as isolate G) isolated from a evaporitic NaCl crystal. Because these organisms are desiccation resistant and gypsum-halite as well as NaCl attenuate UV-radiation, we hypothesized that these organisms would survive in the space environment, better than most others. The organisms were exposed to the space environment for 2 weeks while in Earth orbit aboard the BIOPAN facility. Ground controls time course studies were tested in a space simulation facility. All samples were compared to unexposed samples. Survivability was determined by plate counts and the most probable number technique. DNA breakage was determined by labeling breaks in the DNA with ³²P followed by translation. Results indicate that the osmophilic microbes survived the 2 week exposure. The major cause of cell death was DNA damage. The number of strand breaks in the DNA from vacuum UV exposed cells was greater than the vacuum only exposed cells. Based on these data we have hypothesized that these organisms survive due to their pigments, salt environment and desiccation resistance.

THE ORIGINS OF THE TRANSLATION MACHINERY

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Detailed comparisons of recently completed microbial genome sequences reveals that the components of the translation machinery are extremely conserved and in many cases distributed throughout the Archaea, the Bacteria and the Eukaryota. This strongly supports the notion that translation originated well before the last common ancestor that is defined by 16S rRNA sequence comparisons and therefore is an extremely ancient process. The prebiotic synthesis of peptide bonds on the early Earth may have occurred in a number of ways in the absence of ribosomes. What is unique about translation is the fact that it allows a template directed synthesis of defined sequence peptides and thereby makes the existence of a complete genetic apparatus advantageous. The essence of this modern translation system in turn is that the key component, the transfer RNA (tRNA) can simultaneously interface the RNA world via the codon/anticodon interaction with the peptide world via the fact that the distal portion of the tRNA is aminoacylated. Although modern ribosomes are very complex in terms of size and number of components, a key issue for exobiology is how RNA molecules carrying amino acids came to participate in peptide synthesis. Perhaps the most obvious scenario is that a simplified tRNA molecule which could have existed in even a limited scope RNA world would be capable of carrying amino acids and participate in peptide bond synthesis in the absence of ribosomes. It has already been shown that small RNAs of this type can be aminoacylated. Our immediate goal is to extend this result by demonstrating that once charged such RNAs can also participate in peptide bond formation. As a first step in obtaining this objective we have verified several earlier results which suggested, but did not convincingly establish, that charged tRNAs can in fact participate in peptide bond formation in the absence of ribosomes. Experiments utilizing charged leucine tRNA will be described. The results show that in fact dipeptide synthesis is obtainable in two ways. In the first, the leucine tRNA is incubated with the leucyl tRNA synthetase for periods of time significantly beyond those required for aminoacylation and dipeptide bond formation is shown to occur. One might thus envision translation as arising from primitive synthetases which can both charge an RNA and catalyze peptide bond formation once the RNA is charged. Regardless of the significance of this result, proper controls must be used to show that peptide bond formation in the absence of enzymes is not due to extended exposure of aminoacylated RNA to the synthetase. We have most recently shown that charged tRNAs can participate in dipeptide formation in the absence of both synthetase and ribosomes. In order to accomplish this a dipeptide Ala-His is used as a catalyst/co-factor. The use of similar catalyst/co-factors such as His-Ala and His alone do not facilitate significant peptide bond formation. Studies of the effect of pH have provided some insight to the nature of the reaction.

THE CASE AGAINST COMETARY ORIGIN OF THE OCEANS

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Atmospheres are found enveloping those planets and satellites best able to hold them. Apparently, the existence of an atmosphere depends as much on escape as it does on supply. A consequence of this view is that volatile supplies were probably much greater than the atmospheres that remain. The likeliest candidates are sources associated with the major events of planetary accretion itself, such as volatile-rich planetesimals or direct gravitational capture of nebular gases. Late-accreting volatile-rich veneers, either asteroids or comets, seem attractive but present quantitative difficulties. Comets in particular appear to be quantitatively inadequate. Only one comet in three million hits Earth. For Earth to accrete an ocean of water through comets, some 3000 Earth masses of comets must have been

scattered to the Oort Cloud or beyond. This is excessive. This difficulty applies to Uranus-Neptune planetesimals as well as to a putative massive early Kuiper Belt. Objects falling from a much augmented ancient asteroid belt remain a viable option, but timing is an issue: can the depopulation of a massive asteroid belt be delayed long enough that it makes sense to talk of asteroids as a late veneer? Another appealing candidate population of volatile-rich objects for the inner solar system are scattered planetesimals associated with the accretion of Jupiter, for two reasons: (i) before there was Jupiter, there was no object in the solar system capable of expelling comets efficiently; (ii) the cross-section of the inner solar system to stray objects was greater when there were many planetesimals.

ORGANICS IN SPACE: FROM STARDUST TO PLANETESIMALS

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An ongoing observational research effort to investigate the nature of organic solid-state materials in space has resulted in the discovery of remarkably similar absorption features, attributed to aliphatic hydrocarbons, among interstellar dust clouds in our own galaxy, dust embedded distant galaxies, and the Murchison meteorite. Comparisons between the infrared observations and laboratory processed organic residues suggests that energetic processing of simple ices (such as H₂O, CO, CH₃OH, NH₃, and/or N₂) results in materials similar to those seen in space. Observations at other near-infrared wavelengths have revealed absorption features from some nitrogen-bearing species, and similar comparisons are underway between interstellar dust and laboratory residues in order to learn about the production pathways and the identity of these organic solids. Primitive solar system bodies, such as Kuiper Belt comets, have also been observed spectroscopically, and their relationship to interstellar precursor materials is intriguing. Latest results from these efforts will be presented.

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INTERSTELLAR PRECURSORS OF METEORITIC ORGANIC MOLECULES

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The early Earth may have obtained most its volatile material from the arrival of meteorites and comets at its surface. Some of this matter was accumulated in the form surviving organic compounds. Determining the most likely distribution of meteoritic and cometary organic molecules that could seed primitive planets is a major research goal for Exobiology since it sets the initial conditions for, at least part of, their phase of prebiotic chemical evolution. Sun-like stars form by the gravitational collapse of dust and molecular cloud gas, leading to the formation of a protostar surrounded by an accretion disk

from which planets, comets, asteroids and other debris eventually form. These dark clouds are thus a pivotal phase in the galactic evolution of the biogenic elements in that the chemical processing that occurs in them provides the raw organic material for meteoritic and cometary processing. A coherent theoretical picture of the development of organic complexity from interstellar biogenic material to the beginning of prebiotic evolution, based upon observations and measurements of the chemical composition of primitive Solar System organics, and of dense molecular clouds, is being developed.

In this theory, the organic molecules observed in dense molecular clouds are either the direct products of grain surface reactions or derive from secondary gas phase reactions amongst surface products. A study has been completed of the deuterium fractionation ratios expected from grain surface reactions involving atom additions. It was found that the observed gas phase interstellar D/H ratios in CH₂DOH and CH₃OD are lower than expected solely from formation on grains and that chemical reactions must also be forming CH₃OD in the gas. Recently, a significant step towards calculating the molecular evolution of grain mantles in a correct, self-consistent, manner has been made. The need to correctly account for the stochastic nature of gas-grain interaction in molecular clouds is leading to a new way of performing astrochemical calculations. The general surface reaction scheme, based on the principle of organic radical stability, has been extended to consider oxidation and nitrogen atom additions to carbon chain radicals. It was found that the organic ring molecule ethylene oxide, recently-discovered in the interstellar medium, arises naturally from this extended scheme.

WHAT BIOPOLYMERS ARE EXPECTED IN EXTRATERRESTRIAL ENVIRONMENTS

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To extrapolate from biochemical structures found in terrestrial life to those that might be found extraterrestrially, one must identify structures in contemporary terrestrial biochemistry that are unique chemical solutions to challenges faced by the general living system. Research on terrestrial nucleic acids shows some structural features that are likely to be universal, and others that are not. The design of probes for planetary missions to detect extraterrestrial life is discussed.

TOWARD RNA - THE MINERAL INDUCED PHOSPHORYLATION OF GLYCOLALDEHYDE

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Conceptual studies of molecular evolution have recently focused on an initial role of RNA or similar precursor molecules, mainly due to the catalytic properties of RNA. The application of geochemical and geophysical constraints further strengthen this concept. One factor is the relative ease with which parent molecules of sugars, such as formaldehyde and glycolaldehyde, are formed in experimental model atmospheres that, at least partly, satisfy geophysically and geochemically imposed constraints

and thus are based on the recognition of carbon dioxide and nitrogen as likely major components /11/.

Another factor, contributing to the geochemical consideration of the RNA world concept is the charge imparted by the phosphate ion. This excess negative charge makes it possible to achieve high, reactive concentration on surface active minerals starting from extensive dilution in the hydrosphere /1-3/. Finally, single aldehyde phosphates are found, upon sorption in bilaterally surface active minerals to readily aldomerize to form sugar phosphates /4/. Testifying to its importance in biopoesis, phosphate is found intimately associated with the earliest traces of life on Earth /9/.

The major objection against nucleosides and nucleotides as prebiological molecules has in the past been the apparent lack of a process that, from a wide variety of aldehydes and aldehyde derivatives, could preferentially give rise to a single, ultimately functional species. This particular objection was overcome in principle with the demonstration of mineral-induced selective formation of the hexose-2,4,6-triphosphate diastereoisomer altrose from glycolaldehyde phosphate, in high yield, from aqueous solution at pH 9 /4/ and also the production at near-neutral pH of pentosephosphates (~41% ribosephosphate) from glyceraldehyde-2-phosphate and glycolaldehyde phosphate /12/.

Important remaining problems concern the initial phosphorylation of the simple aldehydes involved /7,8/ and the formation /5,6/ and attachment of nucleobases to the sugars. The phosphorylation problem has now been approached by a process that involves reactants that are produced in geochemically plausible, simulated primordial environments, and brought to reactive concentration by sorption in surface active minerals /1,2,10/. This process of spontaneous, mineral assisted phosphorylation of glycolaldehyde is the main subject of the present report.

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MARS SAMPLE RETURN QUARANTINE PROTOCOL WORKSHOP

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With the possibility of a Mars Sample Return Mission launch as early as 2005, there is renewed interest in, and a sense of urgency about, the requirements for Planetary Protection that might be imposed on such a mission. In Spring 1997, the Space Studies Board issued a report dealing with Mars Sample Return issues. One of the recommendations of this study was that samples returned from Mars should be contained and treated as though potentially hazardous until proven otherwise. This issue was examined further in a Quarantine Protocol Workshop held at NASA's Ames Research Center, June 4-6, 1997.

The objectives of the workshop were: 1) Given procedures employed during the lunar program, develop up-to-date containment procedures, a methodology to detect biological materials, and a methodology to determine if Mars samples are hazardous; and 2) For each set of procedures, identify research and technology needs to specify more detailed procedures. The containment sub-group considered technology requirements to prevent escape of potentially hazardous materials in the Mars sample and evaluated currently available technology and procedures for facility testing and personnel training. The life detection sub-group considered techniques available for detection of biological entities and/or organics in returned samples and examined test priorities and sequences. The hazard determination sub-group focused on methods to determine pathogenicity of Mars samples and evaluated other issues including shortcomings of this approach and criteria or conditions for distribution of the sample.

PLANETARY PROTECTION AND MARS SAMPLE RETURN: FROM NOW THROUGH LAUNCH AND BEYOND

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The public's current fascination with space exploration and its concerns about environment, health and safety all but ensure that plans for returning samples from Mars and handling them on Earth will generate considerable attention. The future success of a 2005 Mars sample return mission will require consideration of not only the scientific and technical aspects of the mission but also the public and legal contexts in which mission plans will be scrutinized. To be responsive to legal requirements and legitimate public concerns, planetary protection must be integrated early into all phases of the mission design. In addition, NASA must keep other government agencies and the public informed throughout the decision making and review process and ensure that quarantine, handling and testing protocols for martian samples on Earth will be stringently followed.

With legal and public contexts in mind, recent research has focused on several important aspects of mission planning in order to anticipate and perhaps minimize future external impediments. Among the areas that have received special attention recently are: 1) consideration of the environmental impact statement and supplemental launch approval process, both of which will require extensive documentation and public review; 2) identification of legal ambiguities and scientific uncertainties that could complicate mission review and approval; 3) developing a systematic, updated testing protocol to determine whether returned martian materials are biohazardous; and 4) studying public risk perceptions and responses to preliminary sample return plans. Information from these areas will be helpful in fulfilling legally required steps in the launch approval process for a sample return mission.

Moreover, the information will help in anticipating problems areas and legitimate public questions, as well as prepare for legal challenges to sample return plans should they arise.

**THE ABUNDANCE OF ^{13}C IN MARINE ORGANIC MATTER
AND ISOTOPIC FRACTIONATION
IN THE GLOBAL BIOGEOCHEMICAL CYCLE OF CARBON
DURING THE PAST 800 MA**

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For the late Proterozoic and earliest Cambrian, the new records of $^{13}\delta_{\text{org}}$ and of the fractionation of ^{13}C associated with fixation of CO_2 by phytoplankton, estimated from $^{13}\delta_{\text{org}}$ and $^{13}\delta_{\text{carbonate}}$, are based on results compiled from the literature and on new analyses and stratigraphic correlations developed by Grotzinger, Hoffman, Kaufman, and Knoll at MIT and Harvard. For the Paleozoic and most of the Mesozoic, the records are based on results compiled from the literature and on new analyses of carefully selected carbonates by Veizer and coworkers at Bochum and Ottawa. For the Cretaceous and Cenozoic, the record of $^{13}\delta_{\text{org}}$ is based on a new compilation of data from the Initial Reports of the various international programs in ocean drilling, with attention to revisions of stratigraphic assignments. For this same interval of time, the record of $^{13}\delta_{\text{carbonate}}$ is based on Shackleton's analyses of total sedimentary carbonate.

Although the records of both $^{13}\delta_{\text{org}}$ and $^{13}\delta_{\text{carbonate}}$ are quite intricately structured, a picture of remarkable simplicity emerges when they are viewed in the context of recent studies of marine phytoplankton (particularly by Bidigare, Laws, Popp, and coworkers at Hawaii). For most of the past 800 Ma, fractionation of ^{13}C has not differed significantly from the maximum set by the physiology and enzymology of marine algae. However, between 550 and 520 Ma (according to a time scale which places the end of the second Varangian Ice Age at 575 Ma and the boundary between the Nemakit-Daldyn and the Tommotian at 534 Ma) the fractionation declined from the maximum by about five per mil. A second decline has long been recognized in the Neogene. The new record shows that it begins abruptly about 29 Ma ago (mid-Oligocene) and that its magnitude increases almost linearly with time, maximizing presently at eight per mil. These declines are probably due to some combination of increased rates of planktonic growth (due to invigoration of oceanic circulation and consequent fertilization of surface waters) and decreases in the abundance of carbon dioxide in the ocean and atmosphere. For the more recent episode, the range of possible variations would include, for example, either constant rates of growth and a 3.6-fold decline in P_{CO_2} or a trebling in growth and a 2.5-fold decrease in P_{CO_2} .

MOLECULAR BIOMARKERS FOR CYANOBACTERIA

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The evolution of oxygenic photosynthesis within the cyanobacterial lineage was one of the most important events in Earth's history. Cyanobacteria diversified and evolved to dominate the early biosphere as witnessed by microfossil assemblages. A crucial means to understand these ancient ecosystems are the modern microbial mats that survive today in many and diverse environments. By studying representative mat organisms in pure culture, insights into the dynamics of mat community structure can be gained. Studies of hydrocarbons extracted from ancient sediments can provide firm connections to modern biology by linking diagnostic molecular fossils, i.e. biomarkers, to specific groups of source organic. In addition, understanding the function and influence of environmental factors on the synthesis of such biomarker molecules within the source organism can extend our knowledge of this ancient organic carbon record. To this end we are presently studying a group specific lipid biomarker for the cyanobacteria, mid-chain, methyl branched alkanes.

A variety of branched alkanes have been isolated from modern cyanobacterial mats. These generally consist of a C₁₆ to C₁₉ hydrocarbon chain with a single methyl group (MMA) at the 6-, 7-, or 8- position (e.g. 7-methylheptadecane). In some instances dimethylalkanes (DMA) with similar chain lengths and methyl positions have also been identified. The presence of MMA in cyanobacterial cultures has been well documented, however, we have only recently identified a C₁₉ DMA with methyl groups at 7,11- or 7,10- in a UTEX culture of *Phormidium luridum*. Quite remarkably, we found that *P. luridum* DMA were only synthesized when the culture was grown with low dissolved inorganic carbon (DIC). Cells grown with atmospheric levels of CO₂ (0.4 mM) contain DMA while cells grown with 1% CO₂ (18 mM) have mostly *n*-C₁₇. The *Phormidium* genus comprise fine, filamentous cyanobacteria which dominate mat formation in the mid-temperature zone (below 55° C to ~30° C) in Yellowstone National Park. *Phormidium* isolated from these mats also synthesize DMA, however, the DIC level does not in itself appear to be a controlling factor in DMA expression in these isolates. In the *Phormidium* mats found at Fountain Paint Pots in YNP, only low levels of DMA are detected in mats submerged in the high DIC waters (6 mM) of these siliceous hot springs, however, dramatically higher levels of DMA were detected in a closely adjacent, sub-aerially exposed mat analog. The subaerial mat now exposed to atmospheric CO₂ levels was also at a much lower temperature as witnessed by increased levels of polyunsaturated fatty acids. These results suggest that DMA synthesis is controlled by a variety of environmental factors affecting membrane function and point to the potential for pure culture studies to provide insights for interpretation of the molecular fossil record.

THE MARTIAN CARBON CYCLE AND IMPLICATIONS FOR THE $\delta^{13}\text{C}$ VALUE OF THE ATMOSPHERE

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In between measurements of the martian atmosphere, precise laboratory measurements on the SNC meteorites, thought to come from Mars, and the possibility of a direct sample return mission, we are

getting data on the carbon isotopic system for Mars. The question then becomes, what do these measurements mean? In order to understand the results, it is necessary to consider what happens to carbon on Mars.

Unlike on the Earth, carbon does not cycle through the martian environment. Instead, primordial carbon is out-gassed from the mantle into the atmosphere. While it may condense onto the polar caps or in a regolith reservoir, it remains in the atmosphere-cap-regolith reservoir until it is lost. Carbon may either be lost from the planet by sputtering and other exospheric processes, or it may be converted into carbonate. On the Earth, carbonate is eventually subducted back into the mantle and then released again during out-gassing. On Mars, there appears to be little, if any, recycling of carbonate (or other crustal material). This effectively makes carbonate a permanent sink for carbon on Mars. It is also why all the out-gassed carbon is primordial instead of mostly recycled as on Earth. If there was life on Mars, it probably never proliferated like on Earth and never represented the carbon reservoir that is seen on Earth. Thus overall, primordial carbon out-gasses from the mantle into the atmosphere and is then either lost into the atmosphere or permanently sequestered in carbonate.

While the carbon system on Mars is, in many ways, much simpler than on the Earth, it is also significantly different. This means that our intuition for the behavior of the $\delta^{13}\text{C}$ isotopic system cannot be applied to Mars. On the Earth, the ocean acts as a large buffer reservoir for carbon. This, coupled with the continual cycling of carbonate and extremely slow escape processes, means that the $\delta^{13}\text{C}$ value for the Earth generally remains close to a fixed value that does not change with time. On Mars, where this is not the case, the $\delta^{13}\text{C}$ value of the atmospheric reservoir can change with time. Using measurements of the SNC Meteorites, we can make reasonable assumptions for the $\delta^{13}\text{C}$ of the out-gassed source carbon. Then by examining the loss processes, we can create a model of the $\delta^{13}\text{C}$ behavior of the atmosphere over the history of Mars. Using constraints on the current atmosphere from measurements as well as laboratory and numerical experiments on the various loss processes, we find that the martian atmosphere started out quite light and has progressively gotten heavier as the atmosphere evolved.

Our modeling implies that when measuring $\delta^{13}\text{C}$ values for Mars, it is critical to know, not only where the carbon is, but also when it was stored. This is especially true for sinks that acquired their carbon from the atmosphere-cap-regolith system. For example, carbonate from two different rocks formed at different times, but by the same process in similar environments may have significantly different $\delta^{13}\text{C}$ values that only reflect their different formation ages. This effect will be especially important when trying to distinguish biotic and abiotic carbonate since the two may have similar $\delta^{13}\text{C}$ values because the carbon came from different reservoirs or because they formed at different epochs.

DETECTION, FORMATION, AND EVOLUTION OF COMPLEX HYDROCARBONS IN PROTOSTELLAR CORES

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The complex chemical ingredients brought to the early solar system may play an important role in the chemical reservoir of the dust and small bodies that form the planets, and in objects such as comets, which continue to supply material to the planets throughout their lives. To understand the initial chemical environment it is especially important to detect and determine the types and abundances of complex hydrocarbons produced during protostar and protostellar disk evolution. We have begun a systematic program to search for complex hydrocarbons and prebiotic molecules in protostellar cores using the radio emission at centimeter wavelengths characteristic of heavy molecules in a low temperature environment. These hydrocarbons and nitriles have a direct bearing on the issues within

exobiology and the origin of life. We report on our progress to date, including the first detections of the longest cumulene carbene and linear carbon chain radicals.

The cumulene carbenes, acetylenic chains, and linear carbon chain radicals are important components of hydrocarbon chemistry in low mass protostellar cores. Their detection and characterization is important for determining the hydrocarbon chemistry. We made the first astronomical detection of the long chain cumulene carbene, H_2C_6 , in a protostellar core from observations of two of its rotational transitions (Langer et al. 1997) in TMC1 and here we also report the detection of the carbon chain radical C_8H . We also observed the shorter cumulene carbene chains H_2C_3 (propadienyldene) and H_2C_4 (butatrienyldene) and several other complex molecules, including HC_9N , HC_7N , C_5H , C_7H , and $c-C_3H_2$, to shed light on the hydrocarbon chemistry. We compare the observed abundance ratios with to chemical models appropriate to the protostellar core.

All these observations were made with NASA's Deep Space Network (DSN) 70 meter antenna at Goldstone, CA. The cumulene carbenes are distributed similarly to those of other complex carbon compounds, such as $HC_{2n+1}N$ and C_nH , but differently from the cyclopropenyldene ring $c-C_3H_2$. We compare the observed ratios to gas phase chemical models appropriate to cores. The fractional abundance of H_2C_6 relative to H_2 is about 3×10^{-11} and that of H_2C_4 about 8×10^{-10} . The H_2C_6 abundance is in reasonable agreement with gas phase chemical models for early evolutionary stages while the H_2C_4 is more abundant than predicted.

This research was conducted at the Jet Propulsion Laboratory, California Institute of Technology, under support from the National Aeronautics and Space Administration.

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ANALYSIS OF THE CARBONACEOUS COMPONENT OF COMET HALLEY DUST

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Comets consist of frozen water, organic and inorganic compounds, and they may have contributed to an early inventory of prebiotic compounds on the primitive Earth and to the reservoir of liquid water on our planet. Comets probably had dual influences on the origin and evolution of life, on one hand, they provided a source of precursors for biochemical while on the other hand their impacts caused severe environmental perturbation. Hence, characterizing the nature and flux of cometary organic material is an integral aspect for understanding life's origins and evolution.

In this work we discuss the compositional groupings obtained by cluster analysis of the carbonaceous component of comet Halley dust. A few basic types of compounds are identified, and we hypothesize that they are essential 'building blocks' which in various combinations give rise to the variety of compositional types observed in cometary dust.

Mass-spectra of about 5000 individual submicron cometary grains were obtained during fly-by missions to comet P/Halley in 1986 [1]. It has been established that cometary dust is extremely rich in organics (~50% by mass). CHON grains, dominated by C alone or in combination with H, O, N, were studied by cluster analysis which revealed more than 30 distinguishable types of grains [2]. We applied the same procedures of cluster analysis to study the composition of the organic component of Mixed particles which are assemblages of organic and inorganic components. These particles represent about 50% of the population of comet Halley dust grains.

In most cases, the carbonaceous component of Mixed particles can be characterized as a multicomponent mixture of carbon phases and organic compounds. Some compositionally simple types identified by cluster analysis are the same as previously found in CHON grains: elemental carbon ([C]-group), hydrocarbons ([H,C]-group), polymers of carbon suboxide and of cyanopolynes. The proportions of all these species are similar in CHON and in Mixed grains.

In addition, polymers of formaldehyde, of hydrogen cyanide and various unsaturated nitriles appear to be present in Mixed particles. Note that the relative abundance of N is higher in Mixed particles than in the previously analyzed CHON group. Some H-containing species observed may form from carbon suboxide and/or cyanopolynes polymers by hydrogenation on grains in the interstellar medium [3]. Finally, some simple ices are observed in individual grains and mixed with organic compounds. These icy grains may survive at the distance of ~10–15 thousand km from the nucleus if they were initially emitted as relatively large particles (> 10 Å) [4].

We conclude that the chemical make-up and the overall variety of dust grain types are consistent with the interstellar grain model [5].

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THE STRUCTURE OF EXTRATERRESTRIAL WATER ICE

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Vapor-deposited amorphous water ice plays an important role in the natural history of the biogenic elements. Such ice is observed spectroscopically as a frost on interstellar dust in dense molecular clouds, and constitutes the bulk of matter in comets. The initial association of the biogenic elements occurs within the icy mantles of grains in cold molecular clouds, and it is here that the first organic compounds are formed. Ultimately, these materials were trapped within icy planetesimals, and were most likely transported to the early Earth within comets or cometary dust.

Nearly all of the properties of extraterrestrial ices (chemical reaction rates, volatile retention and release, vaporization behavior, thermal conductivity, infrared spectral characteristics and the like) are a direct consequence of ice structure. However, the characterization of astrophysical ices and their laboratory analogs has typically utilized indirect measurements which yield phenomenological interpretations.

When water ice is vapor-deposited at 14° K and warmed until it volatilizes in moderate vacuum, the ice undergoes a series of amorphous to amorphous and amorphous to crystalline structural transitions which we have characterized by diffraction methods. These structural transitions correlate with and underlie many phenomena observed in laboratory infrared and gas release experiments.

The elucidation of the dynamic structural changes which occur in vapor-deposited water ice as a function of time, temperature and radiation history allows for the more complete interpretation of remote observations of astrophysical ices and their laboratory analogs.

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THE MECHANISM OF AMINE-CATALYZED HYDROLYSIS OF RNA

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Nucleophilic attack on the phosphorus atom of a phosphate diester by a hydroxyl group is central to the cleavage and ligation reactions that are carried out by ribozymes. This reaction occurs also in the base or RNase-catalyzed hydrolysis of RNA, and may have been involved in the *de novo* formation of RNA in prebiotic times.

This reaction is known to be catalyzed by amines, particularly alkanediamines, yet the mechanism of this catalysis has been a subject of controversy in recent years. We have investigated the imidazole-catalyzed hydrolysis of an analog of RNA, the dinucleoside monophosphate 3',3'-UpU. This dinucleotide is particularly interesting as a model for ribozyme action, for the leaving group is the 2',3'-diol of a nucleoside, just as it is in many ribozyme-catalyzed transesterifications. This is a better leaving group than the 5'-OH of a normal 3',5'-dinucleotide, and so the reaction of our model compound takes place about twenty times faster than for the normal dinucleotide.

We have studied the general species-catalyzed cleavage of 3',3'-UpU in imidazole buffers under carefully controlled conditions, and find that if the polarity of the solvent is held constant as the concentration of buffer is varied, the cleavage reaction shows simple general base catalysis. This is in contrast to the anomalous behavior reported earlier for 3',5'-UpU by Breslow and co-workers, on which they based a series of mechanistic suggestions. Some of their curved plots appear to be artifacts of their experimental method.

However, in spite of the mechanism of amine-catalyzed cleavage now appearing to be simple general-base catalysis, earlier work from our laboratory suggests that the actual mechanism of amine-catalyzed hydroxyl attack on a phosphate diester involves the kinetically equivalent protonated amine plus the deprotonated hydroxyl group. These results are guiding our search for amine catalysts that can improve the yield of RNA oligomers in the *de novo* formation of RNA from nucleoside 2',3'-cyclic phosphates under simulated prebiotic conditions.

INORGANIC SOLIDS AND THE ORIGINS OF LIFE

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Inorganic solids would have provided opportunities for adsorption and concentration, ordering, catalysis and photochemistry not available to materials in solution, and we are exploring some of these possibilities. We have concentrated so far on layered double hydroxides (LDH's), of general type $M(II)_1-xM(III)_x(OH)_2Y_x$ which are naturally occurring ion exchangers and base catalysts, and on the solid state photochemical reduction of carbonate by iron(II).

Layered double hydroxides containing 10 atom % M(II) as iron(II) and incorporating ^{13}C -labeled carbonate, when subjected to UV light, turn darker but generate only traces of formaldehyde (detected by GC-MS as its 2,4-dinitrophenylhydrazone). Iron(II) carbonate itself, under the same conditions, is converted to carbonate green rust [iron(II) iron(III) hydroxide carbonate, itself a member of the LDH family], but again the production of formaldehyde is negligible. Manganese(II), chosen because it could in principle act as the source of two electrons per ion, was without effect either on its own or in the presence of iron(II). We intend, however, to search for other products from these reactions.

Layered double hydroxides readily adsorb ferrocyanide (which we regard as a possible prebiotic species under closed basin conditions) from solution. At high pH, carbonate displaces ferrocyanide from the bulk (but not from the surface) of the LDH particles. In addition, ferrocyanide readily forms insoluble products with magnesium, which can incorporate Group 1 cations, with a possible preference for ammonium. We have evidence that the reaction between ammonium magnesium ferrocyanide and formaldehyde gives rise to a wide range of products, and intend to explore the nature of these, the lower concentration limits for their formation, and which components of the system are necessary for these reactions to take place.

THE CHEMISTRY, MINERALOGY, AND SPECTROSCOPY OF THE BIOGENIC ELEMENTS IN MARS SOIL ANALOGS

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Susan White
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Characterization of the surface of Mars is part of an international effort to determine "whether life ever began on Mars, and if so, in what form". A crucial and key step in the establishment of the early history of abiotic evolution on Mars is the measurement of the concentrations and understanding of the

geological cycles of the six major biogenic elements, hydrogen, carbon, nitrogen, oxygen, sulfur, and phosphorus on the surface of Mars. Laboratory studies to evaluate the reactivity and mineralogy of the biogenic elements in a model Mars soil matrix are being conducted. Experimental and theoretical approaches are being used to study the spectral fingerprints of the biogenic element minerals in order to constrain their detectability limits for remote sensing observations. Studies are focusing on the effects of the biogenic elements on the reactivity (surface acidity and redox potentials) of Mars soil analogs and on simulations of the Viking Biology experiments. The broad objectives of these experiments are to constrain the mineralogy of the biogenic elements in model Mars soil matrices, to suggest scenarios for their distribution and transformations in the martian environment, and to support interpretation of remote sensing and Mars surface probing data obtained from orbiters and landers.

Reflectance spectroscopic evaluation of mixtures of the biogenic elements in a Mars soil matrix has been initiated using both physically prepared mixtures and those prepared by acid weathering procedures in the laboratory. For the physical mixtures, initial interpretation of the visual and near-infrared wavelength region (0.25-2.5 mm) spectra indicates a subtle increase of the overall reflectance at the highest concentrations of sulfate and in a mixture of all salts. In the far-infrared region (2.5-25 mm), distinctive spectral features are visually observed for carbonate and sulfate salts at all concentrations, but no distinctive spectral features are seen for the nitrate or phosphate. Additional spectral analyses are planned in the far-infrared to investigate whether subtle spectral features will help identify the presence of the nitrates and phosphates.

Mars soil analogs were prepared by acidolytic weathering of a partly palagonitized volcanic tephra by adding varying inputs of sulfuric, nitric and hydrochloric acids, at levels of addition covering the range from zero to the corresponding biogenic element concentration found (or estimated) in Mars soil and beyond. These acidified Mars soil analogs were characterized by a titration-extraction procedure which measures solid-surface and solution acidity and by X-ray diffractometry. The results show that volcanic palagonitized tephra, "artificially-weathered" by addition of various acids, is stabilized at pH levels buffered by the Al and Fe hydrolysis products. Titration curves show that the total final acidity is practically equal to the added acidity, the majority being present as hydrolytic species of Al, Fe and Mg released from the tephra minerals.

EARLY EVOLUTION OF LIFE IN NON-MARINE ENVIRONMENTS

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Arizona State University

The Earth today contains about 1.3×10^{22} g of NaCl stored as subsurface salt deposits in sedimentary basins and probably an even greater amount in continental brines and ground waters. If all this salt were returned to the ocean the salinity would rise by at least 60%. Assuming that Cl was outgassed with water, the early oceans may have been this saline until significant halite was removed by evaporite deposition in sedimentary basins on continental platforms. Ideas vary regarding when such platforms became established and when huge accumulations of salt were finally sequestered, but it may not have happened until sometime in the Proterozoic. Until oceanic salinity was drawn down, early evolution of life may have been especially active in the lower salinity, non-marine waters in lakes, rivers, and soils. These environments sit high on continents and their deposits are preferentially eroded away relative to marine deposits. However, some non-marine deposits have been preserved, and many contain horizons conducive to the preservation of microfossils. The purpose of this project is to identify silica and carbonate that formed in early sub-aerial and other non-marine environments and explore further the newly emerging fossil record of life on land in the Precambrian.

Chert-bearing carbonate strata that undergo intense weathering yield a distinctive paleokarst deposit composed of insoluble chert, clay, and secondary low ^{18}O carbonate and silica that are deposited from meteoric waters during the event. ^{13}C -depleted CO_2 is injected into the ground waters by vegetated surfaces and gets incorporated into the secondary carbonate, thereby providing an isotopic signature of sub-aerial organisms. Microfossils of probable cyanobacteria have been found in the associated secondary silica in paleokarsts as old as 1200 m.y. ^{13}C depletions are comparable to modern karsts suggesting a very significant subaerial biomass at that time. More complicated pseudofossils in this silica are currently being evaluated for possible biogenicity and even older horizons will be examined.

Quartz-filled amygdules and veins in silicic volcanic deposits are normally assumed to be of hydrothermal origin. However, recent oxygen and hydrogen isotope analyses show that much of this silica actually formed at surficial temperatures as weathering products of the silica-rich volcanic glasses. Modern examples near the surface are often little biospheres containing cyanobacteria and other microorganisms. The preservation of such organisms in this type of silica is currently being examined and ancient examples are a new target material for exploring the fossil record of life on land in the Precambrian and possibly on Mars. Calcite alteration veins in terrestrial basalts are being similarly examined and may provide easily accessible target material for future sample returns from Mars.

THE DIVERSITY OF THE OUTER PLANETARY SYSTEM

H. Levison* and J. Lissauer

A set of plausible outer planetary systems were constructed using direct numerical integrations. Included in these simulations were the effects of the solar nebula. This included the accretion of nebular gas in order to form Jupiter-like planets. It was found that some sort of dissipation was required for time scales longer than 10 million years in order to construct systems like ours. The number of planets can vary from one to seven. Systems with a large number of planets never contain large, Jupiter-like planets, but instead are made up of Uranus-like planets. Stable planetary systems can include planets in mean motion resonances with one another. Perhaps most surprisingly, it is possible to construct stable systems in which that planetary orbits can undergo large, semi-periodic changes.

FORMATION OF THE ASTEROID BELT

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Little attention has been given to the formation and early history of asteroid belts, despite their importance. Asteroids are the source of almost all meteorites, including the primitive carbonaceous meteorites that carry a record of prebiotic chemistry in the early Solar System. Devastating impacts of asteroids, and their probably much larger counterparts in the early Solar System were a major factor in shaping the course of the earliest evolution of life on Earth, and probably in other planetary systems as well. Collision debris in the much more populated early asteroid belt will spiral into the terrestrial planet region by gas drag and make a significant contribution of otherwise rare crustal and upper mantle elements to the Earth's surface.

A central problem in asteroid belt formation is understanding why there is a region in our Solar System that is depleted in mass by a factor of several thousand, as compared with the terrestrial and giant planet regions. To approach this problem, models of the formation of bodies interior to giant planets in

planetary systems have been developed using the same techniques used to study terrestrial planet formation:

- (1) Treatment of planetesimals as analogues of molecules in gas dynamic transport theory,
- (2) $\sim 10^4$ body Monte Carlo evolution of growth evolution of $\sim 10^{24}$ g bodies,
- (3) Numerical integration of ~ 40 larger bodies for times up to $> 10^8$ years.

Assuming an approximately smooth decrease in nebular surface density, the earlier stages of growth lead to an asteroid belt population of ~ 25 bodies as large as Mars or more between Earth and Jupiter within a few million years. Numerical integration shows that, in about half the cases, mutual perturbations, together with resonant long range forces due to the giant planets removes all these large bodies from the asteroidal region on a $\sim 10^8$ yr time scale. Otherwise one or more of these small planets remain between the terrestrial and giant planets. Remnant bodies analogous to Mars are also found. The present asteroids are then the products of collisions between the larger bodies, as well as those of the associated retinue of smaller bodies. The present ~ 5 km/sec relative velocities of the asteroids, their number, position, degree of mixing and size distribution are shown to be consistent with their being consequences of these events.

The above models make the conventional assumption that gas giants postdate the formation of the Mars-sized asteroidal bodies. Recently, A. Boss has proposed that solar system and extrasolar gas giants can form from gravitational instabilities in the disk during the final stages of formation of the central star. We have investigated the effect of this process on the formation of Earth-like bodies and asteroids interior to the gas giants. Preliminary results suggest this process could preclude formation of such bodies, despite the tendency of similar phasing of gas giant perturbations to limit the relative velocity between growing planetesimals.

THE ROUTE FROM INTERSTELLAR TO PROTOSTELLAR ABUNDANCES: EVIDENCE OF VARIABILITY IN THE INTERSTELLAR MEDIUM

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Jet Propulsion Laboratory

We have tested the often-made assumption that there is a steady evolution of nuclear abundances in the Galaxy, which results in a balanced enrichment of the elements considered essential for the evolution of life. Our test consists of making observations, on the scale of a solar mass, which might indicate whether or not the abundances of the nuclides in the interstellar medium are uniform. A finding of non-uniformity would imply that stellar systems with abundances much like the present-day solar system, could have existed already in early Galactic history, nearly 5 billion years before the creation of the Sun.

The particular nuclear abundance ratio chosen for study is $^{17}\text{O}/^{18}\text{O}$: The most precisely determined extra-solar abundance ratio, and one which is known to be evolved by means of production in red giant stars. There is also significant evidence for local enrichment, based on the presence of enriched grains in meteorites, showing anomalous abundances of the oxygen isotopes (Clayton et al., 1977; Huss et al., 1994)

We have completed a study of Rho Oph, a nearby, molecular cloud complex, using the isotope pair most favorable for accurate studies: $^{17}\text{O}/^{18}\text{O}$. We have tentatively concluded that there are, indeed, measurable variations in abundances on solar-mass scales. Our present goal is to confirm this finding, and to extend the result to an examination of the nearest known interstellar molecular cloud:

L1457. The observations were carried out at the Five College Radio Observatory (FCRAO) with their array receiver.

SPECTROSCOPIC STUDIES OF PRE-BIOTIC CARBON CHEMISTRY

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Research in the Blake group supported by the Exobiology program seeks to understand the evolution of molecular complexity in pre-biological environments. The major tool used is spectroscopy, and the program has observational, laboratory, and theoretical components. In our observational work, we combine high resolution (sub)millimeter-wave and IR images from the OVRO/Hat Creek Arrays and Keck telescope with high dynamic range spectra from the ISO satellite to constrain, for the first time, the overall chemical budgets of the biogenic elements during the star formation process. We also have an active observational program characterizing the composition and thermal properties of comets (Hyakutake, Hale-Bopp) and Kuiper Belt Objects.

Imaging with the Millimeter Arrays is designed to probe, at the highest possible angular resolution, the critical coupling of gas phase and grain mantle chemistry in the prebiotic evolution of protoplanetary nebulae. We stress that such aperture synthesis data at "long wavelengths" (compared to optical and near-IR studies which suffer greatly from extinction) is the only general probe of gas-phase chemistry in material that *must* become part of the young star and any attendant planetary system. In our work to date, it is clear that certain species are excellent probes of the structure of out-flowing gas, but that the unambiguous detection of in-falling and rotating gas - material which is dynamically bound to the young star - is difficult even at high angular resolution.

Comets are among the most primitive bodies left over from the planetesimal building stage of the solar nebula, and so their physical and chemical composition provides an important link between nebular and "interstellar" processes. At OVRO, local oscillator settings were optimized to allow access to transitions of HCN, HC₃N, CH₃CN, HNCO, CS, SO, SO₂, OCS, H₂S, HDO, CO, H₂CO, CH₃OH, and HCOOH. Comet Hale-Bopp was detected in each of these molecules during the spring of 1997, and was sufficiently large that millimeter-wave thermal emission from the nucleus itself was detected. This unique data set is the first to image many of these molecules at spatial resolutions characteristic of optical astronomy with the tremendous spectral resolution of radio techniques.

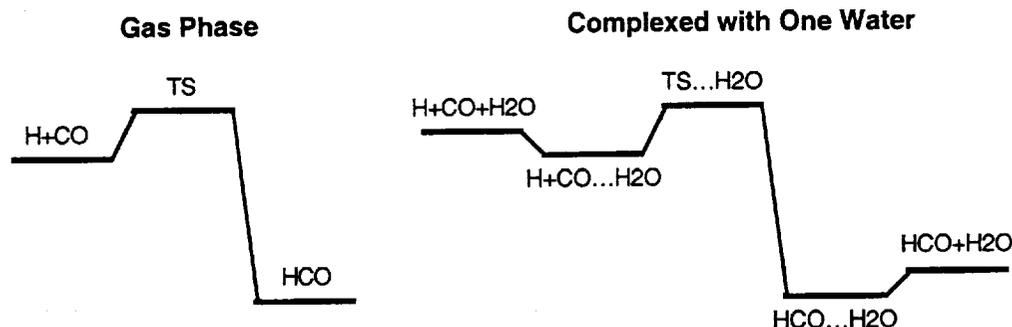
Our laboratory work, performed with mid-infrared tunable diode laser, VUV → mid-IR pulsed field ionization (PFI), and far-IR photomixer/supersonic jet spectrometers that were constructed, in part, with Exobiology support, concentrates on acquiring spectra that will shed new light on the extraordinarily complex prebiotic chemistry of carbon as reflected in interstellar and primitive solar system materials. There are two major targets of emphasis. The first includes small, reactive intermediates such as the vinyl radical, benzyne diradical, and carbenes which are thought to be key components in the synthesis of larger "molecular grains" such as PAHs or carbonaceous grains. The second is the examination of such molecular grains themselves, particularly long chain polyacetylene or cyanopolyacetylene species along with refractory species such as carbide clusters.

THEORETICAL STUDIES OF THE EXTRATERRESTRIAL CHEMISTRY OF BIOGENIC ELEMENTS AND COMPOUNDS

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Gas-grain reactions are thought to play an important role in the formation of molecular species in interstellar and circumstellar clouds. These include known species with important exobiological implications such as alcohols, ketones, aldehydes, and carboxylic acids, as well as candidate species including small amino acids such as glycine. Grain surfaces may influence reactions in different ways: as reaction sites for catalyzing the formation of species that possess high gas-phase barriers or as sinks for excess reaction energy in association reactions without barriers. Grain surfaces also provide nucleation centers for macroscopic accretion and the consequential depletion of elements from the gas phase. The goal of this work is develop new theoretical models for elucidating the mechanisms of important gas-grain reactions that incorporate as much information as possible from accurate quantum chemical calculations.

One of the reactions of greatest interest is the hydrogenation of CO to form the formyl radical HCO, a critical early step in the formation of many larger organic species. The $H + CO \rightarrow HCO$ reaction possesses a very high barrier in the gas phase, but several experimental studies have provided evidence that the process is greatly enhanced on icy surfaces comprised of water or other molecules. We are using correlated *ab initio* molecular orbital methods to investigate the microscopic mechanism by which water modifies the reaction. We are doing this by first considering small clusters, particularly $H + CO \rightarrow HCO$ with one and two water molecules present. Our calculations indicate that water has a negligible impact on the energetics of the reaction, the barrier remaining very high. However, even one water fundamentally alters the form of the potential energy surface (as depicted below) by providing a substrate to which hydrogen can adhere and repeatedly attempt to tunnel through the barrier.

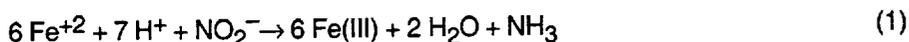


REDUCED NITROGEN ON THE EARLY EARTH

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SETI Institute and NASA Ames Research Center

With current geochemical evidence pointing to a non-reducing atmosphere, the formation of reduced nitrogen on the early Earth, or other planets with a carbon dioxide/nitrogen atmosphere, is problematic. One source of reduced nitrogen starts with the fixation, by shock heating, of nitrogen to

NO followed by photochemical conversion of the NO into nitrite. The nitrite can then be reduced to ammonia by ferrous iron (Reaction 1).*

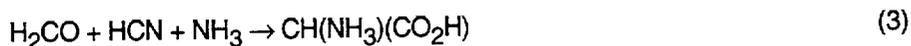


It has been suggested that the reaction of ammonia with nitrite (Reaction 2)



prevents reaction 1 from being a significant source of ammonia on the early Earth. However, whether this is true depends on how the kinetics of reaction 2 compare with other sources and sinks for both ammonia and nitrite. Any evaluation of the importance of various sources and sinks of nitrite and ammonia, and of whether ammonia is likely to be present in significant amounts, requires an analysis of all the kinetic processes affecting these species.

One potential source of amino acids under non-reducing conditions is via the Strecker synthesis, equation 3, utilizing the ammonia produced above.



However, several questions arise. Is ammonia, from the reduction of nitrite by iron(II), compatible with the Strecker synthesis? Will complexation of the cyanide to the iron deactivate one or the other (or both)? Will both of the reactions proceed under the same conditions? Conversely, could a $\text{Fe}(\text{CN})_n^{+(2-n)}$ type species provide some catalytic effect, either for the reduction of nitrite/nitrate or for the formation of amino acids?

The analysis of sources and sinks of nitrite and ammonia found that, under most environmental conditions, the primary sink for nitrite is reduction to ammonia. The reaction between ammonia and nitrite is not an important sink for either nitrite or ammonia. Destruction at hydrothermal vents is important at acidic pHs and at low ferrous iron concentrations. Photochemical destruction, even in a worst case scenario, is unimportant under many conditions but could be important under acidic, low iron concentration, or low temperature conditions. The primary sink for ammonia is photochemical destruction in the atmosphere. Under acidic conditions, more of the ammonia is tied up as ammonium (reducing its vapor pressure) and hydrothermal destruction becomes more important.

The studies on the interactions of reactions 1 & 3 found that; A cyanide/iron ratio of 2:1 or less doesn't prevent the formation of ammonia by the iron(II) reduction of nitrite. However, a cyanide/iron ratio of 4:1 or greater, no ammonia is formed across all pHs. At lower pHs nitrite is reduced to other products. The Strecker synthesis does not appear to be hampered by the presence of iron. The Strecker synthesis and the iron (II) reduction of nitrite to ammonia can be combined to form amino acids from nitrite, iron(II), cyanide, and formaldehyde.

PREFERENCE FOR INTERNUCLEOTIDE LINKAGES AS A FUNCTION OF THE NUMBER OF CONSTITUENTS IN A MIXTURE

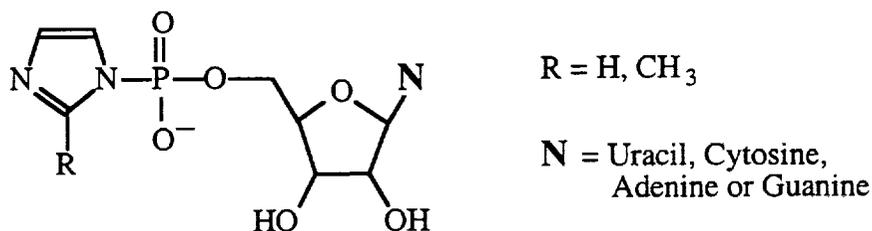
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Phosphoimidazole activated ribomononucleotides (*pN, see structure) are useful substrates for the non-enzymatic synthesis of oligonucleotides. In the presence of metal ions dilute neutral aqueous

solutions of *pN (0.01 M) typically yield only small amounts of dimers and traces of oligomers; most of *pN hydrolyzes to yield nucleoside 5'-monophosphate (5'NMP). An earlier investigation of *pN reactions in highly concentrated aqueous solutions (up to 1.4 M) showed, as expected, that the percent yield of the condensation products increases and the yield of the hydrolysis product correspondingly decreases with *pN concentration (Kanavarioti, 1997).

Here we report product distributions in reactions with one, two or three reactive components at the same total nucleotide concentration. *pN used as substrates were the nucleoside 5' phosphate 2-methylimidazolides, 2-MelmpN with N = cytidine (C), uridine (U) or guanosine (G). Reactions were conducted as self-condensations, i.e. one nucleotide only; with two components in the three binary U,C-, U,G- and C,G-mixtures and with three components in the ternary U,C,G-mixture. The products are 5'NMP, 5',5'-pyrophosphate-, 2',5'-, 3',5'-linked-dimers, cyclic dimers and a small percentage of longer oligomers. The surprising finding was that, under identical conditions, including the same total monomer concentration, the product distribution differs substantially from one reaction to another, most likely due to changing intermolecular interactions depending on the constituents. Even more unexpected was the observed trend according to which reactions of the U,C,G-mixture produce the highest yield of internucleotide-linked dimers, whereas the self-condensations produce the least and the reactions with the binary mixtures produce yields that fall in between. What is remarkable is that the approximately two-fold increase of the percent yield of internucleotide-linked dimers is not due to a concentration effect or a catalyst, but it is due to the increased complexity of the system from a single to two and three components. These observations, perhaps, provide an example of how increased complexity in relatively simple chemical systems leads to organization of the material and consequently to chemical evolution.



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INTERACTIONS OF CARBON COMPOUNDS AND PHOSPHATE WITH PYRITE IN AQUEOUS SOLUTIONS

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Pyrite plays a central role in the chemo-lithotrophic model championed by Wachtershauser /1/. The pyrrhotite-hydrogen sulfide/pyrite (FeS-H₂S/FeS₂) redox couple is assumed to have reduced CO₂ or CO to simple organic compounds. Once formed, these simple C-compounds as well as phosphate are thought to sorb onto the pyrite surface and undergo reactions leading to more complex molecules. Experimental work shows that the FeS-H₂S/FeS₂ redox can reduce CO /2/ and CS₂ (or COS) /3/, but

there is no evidence for direct reduction of CO₂ /4/. Sorption of simple C-compounds and phosphate onto pyrite is based on the notion that the pyrite has a positive surface charge and will accumulate anionic species due to electrostatic attraction. Our research is directed to: (a) evaluate the energetics and kinetics of the reduction of inorganic C1 compounds with the FeS-H₂S/FeS₂ couple as reductant and (b) to determine the effectiveness of pyrite as a scavenger of C-compounds and phosphate.

Thermodynamic calculations were carried out to evaluate the energetics of CO₂ reduction via a sequence of reactions limited to a transfer of two electrons per step. The calculations were conducted for a temperature range of 0 to 300° C (P = 300 bar). The results show that the reducing power of the FeS-H₂S/FeS₂ couple drops with increasing temperature. Furthermore the first step, reduction of CO₂ to HCOOH, is energetically unfavorable. A Frontier Orbital Theory (FOT) analysis shows that the Lowest Unoccupied Molecular Orbital of CO₂ is at an energy level that would require electrons donated from H₂S to the FeS to gain energy. This energy barrier prevents facile CO₂ reduction. FOT analysis provides also insight into the facile reduction of CS₂ and CO. FOT analysis may be useful as a guide for future experimental work.

The surface chemistry of pyrite is complex. The surface charge of pyrite is negative in the absence of added iron between pH 2 and 11, but becomes positive in the presence of dissolved ferrous iron between pH 2-5 and above pH 8. Hence, the iron content of the Hadean ocean may play a pivotal role in controlling sorption of C-compounds. The interactions of C-compounds with pyrite depends on their functionality. Phosphate and phosphorylated compounds are strongly retained on pyrite, while acetate, alanine, and glycine show little interaction. It is noteworthy that phosphate sorption onto pyrite requires that anionic phosphate species overcome electrostatic repulsion as they approach the pyrite surface. This indicates that the phosphate species form a chemical bond with the pyrite surface.

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THE MEENTHEENA CARBONATE, ANCIENT LAKES, FACIES, AND EXOBIOLGY

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H. Paul Buchheim
Loma Linda University

The Meentheena Carbonate Member of the Tumbiana Formation (Fortescue Group; Late Archean) with its abundant and diverse stromatolites and rare microfossils represents an important unit with significant exobiological implications for understanding ancient life in lakes. The Meentheena was deposited some 2715 Ma ago within an intracratonic basin, either as one large lake over 350 km across or in a series of smaller lakes.

A complex picture develops as one analyzes data obtained from a detailed study of the Meentheena. A lithofacies association with repetitive cycles was identified for the unit: from base to top – oolite-flat-pebble conglomerate, rippled oolite, parallel-laminated oolite/grainstone, and shale. Stromatolites

increase in abundance upward in the carbonate part of the lithofacies association and occur in several sedimentary units. Some individual carbonate units and cycles of the lithofacies association could be correlated over 16 km locally, and at least 190 km regionally. Lateral facies changes occur over short distances; however, significant changes occur within a few km where the entire carbonate portion is nearly replaced by shale and rippled tufaceous siltstone and sandstone. Two key stromatolites provide marker beds permitting local and regional correlation. One, laterally-linked, low profile domes, permits regional correlation over 190 km. The other, dense clusters of *Alcheringa narrina*, permits local correlation over 16 km. The lithofacies association is interpreted as a transgressive lacustrine sequence with upward decreasing energy and increasing depth. The basal oolite-flat-pebble conglomerate represents a high energy shallow-water, near shore facies. Increasing depth and lower energy levels resulted in deposition of wave-rippled oolite. The parallel-laminated oolite/grainstone facies (with larger stromatolites) was deposited in deeper water as transgression continued. Finally, deposition of shale dominated the system as depths increased. Dynamic fluctuations in lake depth resulted in incompleteness of lithofacies associations. Similar lithofacies, cycles, and associations are found in the Eocene Green River Formation, a model system for large ancient lakes.

The Meentheena and its stromatolites indicate that during the late Archean microbial life thrived in lakes and, that despite higher atmospheric $p\text{CO}_2$ levels, carbonates preserving aspects of this fossil record can be widespread. It is our suggestion that the search for evidence for ancient life on Mars, include lacustrine deposits with repeated sequences that might represent fluctuating water depths.

MARS STUDIES

H.P. Klein*
SETI Institute

This work began as an outgrowth of participation on the Russian Mars '96 mission, and was initially directed toward two aspects of that mission: involvement in the Mars Oxidant experiment (MOx), which was chosen to be flown on the small lander, and involvement in establishing geological criteria of exobiological relevance for detailed study by the orbiter.

For the first of these objectives, I played a role on the science definition team, paying particular attention to the selection of organic coatings for the MOx. For the second, in collaboration with Ron Greeley of Arizona State University, and Drs. Dave DesMarais and Jack Farmer of NASA Ames, I helped to assemble a list of about twenty sites on Mars for critical study by the orbiter.

With the loss of the Mars '96 mission in November 1996, further participation in that mission was precluded. However, collaboration with Greeley has continued and was extended to include characterization of the Ma'Adim Vallis-Gusev Crater region and of the Ares Vallis region, which was to become the landing site for the Pathfinder spacecraft. Currently, good progress is being made in analyzing the flooding events feeding into the Pathfinder region, and detailed mapping of the Gusev Crater area is continuing. In addition, further analysis of the Viking orbiter data will continue, with the objective of finding additional sites for exobiological study on Mars' surface.

**ABSTRACTS
of
POSTER PRESENTATIONS**

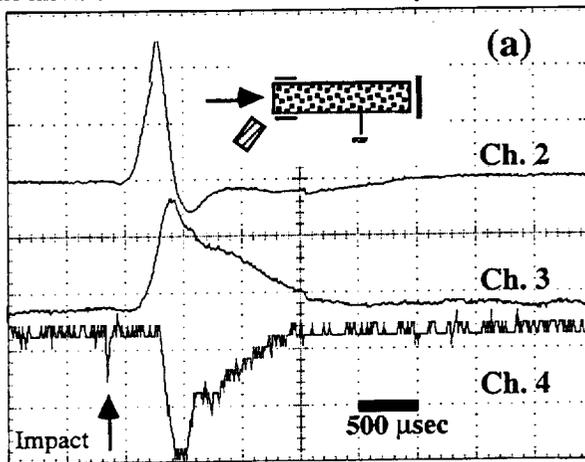
(Shown in alphabetical order by the first author's name)

IGNEOUS ROCKS THAT SPARKLE, CRACKLE AND GLOW Oxidizing Radicals Activated by Low Velocity Impacts

Jerome G. Borucki*, Steven J. Butow, Marshall Lisé, and Friedemann Freund
NASA Ames Research Center; SETI Institute;
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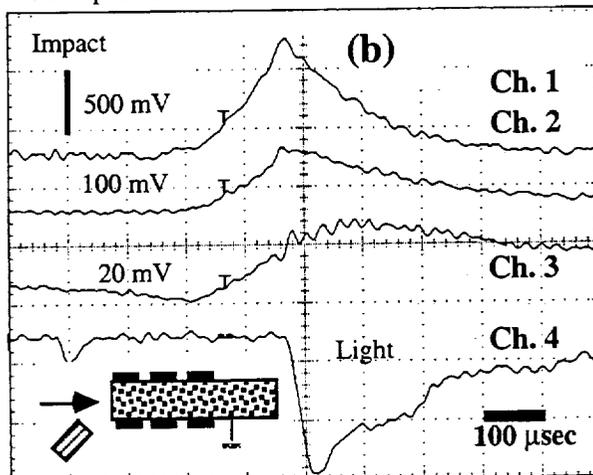
Water dissolves in minerals that make up most common igneous and highly metamorphic. However, the complexity of the dissolution mechanism has only recently been more fully understood. When H₂O becomes incorporated in nominally anhydrous minerals, it forms at first X-OH (with X = Si⁴⁺, Al³⁺ etc.), but X-OH pairs subsequently undergo an internal redox reaction into peroxy links, X/OO/X, plus H₂. These peroxy links are interesting entities: Physically, they are self-trapped pairs of positive hole charge carriers; Chemically, they are two O⁻ radicals held together by a short but labile O⁻-O⁻ bond. The O⁻-O⁻ bond can be thermally broken, leading to highly mobile positive hole charge carriers. Fracture experiments demonstrate that the shock arising from brittle fracture is enough to also cause the O⁻-O⁻ bond to come apart. We set up low velocity (100 m/sec) impact experiments and found that they produce positive hole charge carriers that propagate through our 3/4" diameter, 3" long rock core targets at 330 m/sec. The charge carriers generate positive surface potentials in the range of +0.5 V to +1.0 V, draw currents as high as 0.4 mA, emit electromagnetic radiation in the 1 to 40 KHz

The insets show the core with detector lay-out



Ch. 2: Front end ring capacitor, 200 mV/div;
Ch. 3: Back end plate capacitor, 20 mV/div;
Ch. 4: Front end light emission, 200 mV/div;

The impactor hits from the left at 100 m/sec



Ch.1-3: Three collector electrodes.
Ch 4: Light

range and also emit light. The light is caused by plasma discharges that occur along the surface and along the rim of our rock cores.

This work is relevant to Exobiology. When rocks are stressed during tectonic events leading to microfracture or shocked during earthquakes, positive holes will be generated. Those coming to the surface of the rocks will act as highly oxidizing O^- radicals, capable of "burning" H_2 to H_2O and organics to CO_2 . They may have forced early Life to develop enzymatic defense mechanisms.

FAMILY CALONYMPHIDAE: TERMITE PROTISTS RELEVANT TO EARLY EUKARYOTIC EVOLUTION

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Trichomonads are anaerobic, amitochondriate protists that comprise one of the earliest lineages of eukaryotes. The trichomonad family Calonymphidae, found only as symbionts of termites, displays an evolutionary sequence that can provide insight into the origin and evolution of mitosis while serving as ideal organisms in the search for kinetosome DNA. This family has evolved from ancestral karyomastigont-containing cells (Coronympha, Metacoronympha, Stephanonympha) in which the nucleus reproduces as a unit with the mastigont structures (kinetosomes and undulipodia) to the partial separation of nucleus from kinetosomes (Calonympha) to the complete removal of nucleus from kinetosomes (Snyderella). Calonympha and Snyderella are ideal organisms for the search for kinetosome DNA in that they lack mitochondria, and have cortical kinetosomes separated from nuclei, which can function as internal controls for the presence of DNA.

An 8 minute video showing each of the genera in this family will be presented by Lynn Rothschild*.

HYDROTHERMAL PROSPECTING ON MARS

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On Earth, the surface expression of hydrothermal activity varies greatly in relationship to such things as the tectonic setting, geothermal gradient, geohydrology and secular variations in climate. Our knowledge of the geological expression and spatial localization of hydrothermal systems and their historical importance in the thermal history of Mars is presently poorly constrained and must await a more detailed understanding of martian surface geology and its evolution. Nevertheless, hydrothermal processes have been suggested to explain a number of recent observations for Mars, including hydrous mineral assemblages and D/H ratios of water extracted from SNC meteorites, as a mechanism for the removal of CO_2 from the martian atmosphere and its sequestering in the crust as carbonates, and the origin of nontronite clays in martian dust and iron oxide-rich spectral units on the floors of some chasmata. Numerous examples have been noted of martian channels formed by discharges of subsurface water, and hydrothermal processes are a suggested mechanism for aquifer recharge needed to sustain long term erosion by sapping channels.

Simple channel systems associated with potential heat sources, such as impact craters or shallow igneous intrusives and volcanic constructs, provide the present focus in targeting sites for hydrothermal prospecting during upcoming mission opportunities. Most of the work to date has been based on visible imaging obtained by Viking. But reliable site evaluations also require information about surface composition. A preferred method is high spatial resolution, mid- or near-IR spectroscopy, tools of choice for mineralogical mapping on Earth. Comparative studies of Mars imaging data and hydrothermal systems on Earth have focused our site selection efforts on a number of high priority geotectonic terranes that appear to offer the best targets for ancient hydrothermal systems on Mars. These include the following: impact structures, rifted basins, areas flanking volcanic constructs and shallow intrusives, caldera floor deposits, and features formed by volcano-ground ice interactions in sub-glacial and periglacial environments. Site lists organized around these terrane types will provide targets for orbital imaging during the MGS '96 mission and beyond. The new orbital data will provide a basis for refining site selection priorities for landed missions in 2001 and 2003, as well as a sample return mission in 2005.

ORGANIC CARBON ASSOCIATED WITH CARBONATE IN ALH84001

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MVA Inc.

McKay et al. /1/ suggest the ALH84001 meteorite contains evidence suggesting ancient biological activity on Mars. One line of evidence is the concentration of polycyclic aromatic hydrocarbons (PAHs), frequently produced by the decay of living material, occurring in close proximity to magnetite and sulfide similar in size and shape to those produced by terrestrial bacteria /1/.

We employed the Scanning Transmission X-Ray Microscope at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory to determine the bonding state(s) and the spatial distribution of the carbon in ultramicrotome thin-sections of carbonates and the rims on these carbonates from ALH84001 /2/. Both the carbonate and the rim sections contained carbon-rich regions (other than carbonate), but each gave a different C-XANES spectrum, suggesting the carbon-bearing compound was different in the rim and the carbonate /2/. We then examined the same sections using a Spectra-Tech micro-Fourier Transform Infrared (u-FTIR) spectrometer, on an infrared beamline at the NSLS, to identify the carbon compounds.

The u-FTIR spectra of the rim samples showed a broad absorption near 1000 cm^{-1} , characteristic of silicate glass, and two weaker features at 2918 cm^{-1} and 2850 cm^{-1} . These two features are consistent in position and relative depths with the symmetric and asymmetric stretching vibrations of the C-H₂ in aliphatic hydrocarbons. The u-FTIR spectrum of the carbonate globule showed a narrow absorption at $\sim 1500\text{ cm}^{-1}$, characteristic of carbonate, and a weaker absorption at 2964 cm^{-1} . Two even weaker features appear at 2920 cm^{-1} and 2850 cm^{-1} . The feature at 2960 cm^{-1} is characteristic of the C-H₃ asymmetrical stretching vibration. Although a weaker C-H₃ symmetrical stretching vibration generally occurs near 2870 cm^{-1} , this feature is absent in the carbonate globule spectrum, and is suppressed in certain compounds containing C-H₃ groups. One particularly good spectrum of the carbonate globule sample appears to show a weak, broad absorption over the range 2990 cm^{-1} and 3060 cm^{-1} . If real, this feature could indicate the detection of C-H stretching vibrations of a mixture of PAHs, which would have an absorption near 3030 cm^{-1} .

These preliminary results confirm that high concentrations of organic carbon are associated with carbonate globules and rims in ALH84001, and further confirm the STXM observation that the rim and the carbonate globule contain different types of carbon. The results seem to rule out the simplest form of organic contamination of ALH84001, simple evaporation of an organic-rich fluid, which would be expected to leave the same residue in both the carbonate globules and the adjacent rim material.

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**THE EFFECTS OF AMONG SITE RATE VARIATION ON
PHYLOGENETIC RECONSTRUCTION FROM AMINO ACID SEQUENCES**

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Olga Zhaxybayeva
Kazakh State National University (Planetary Biology Institute fellow)

Systematic artifacts have long been recognized as important complications in phylogenetic reconstruction. The most serious of these is long branch attraction. Two scenarios can yield long branches: (A) some sequences evolve faster due to higher substitution rates; or (B) the long branches can be due to the absence of side branches in some lineages.

Protein sequences are useful for comparisons between distantly related sequences because their 20 letter alphabet in conjunction with substitution bias facilitates the alignment of divergent sequences. Sequence alignment is further aided by highly conserved residues that remain unchanged even between distantly related proteins. In case of nucleotide sequences simulations have been performed to estimate the effect of among site rate variation (ASRV) on phylogenetic inference; however, at present the effect of ASRV on long branch attraction on protein based phylogenies has not been explored.

Using computer simulation to generate sequence data for protein families, we studied the influence of among site rate variation on the performance of phylogenetic reconstruction. The algorithm used for simulation incorporates both among site rate variation and substitution bias. Among site rate variation was simulated using discrete approximations to continuous Gamma distributions with different shape parameters. In the chosen parameter range the simulation was shown to be consistent with maximum likelihood estimation of the shape parameter. The simulation utilized different tree topologies to explore the effect of long branch attraction with data that incorporated substitution bias and different degrees of among site rate variation. While all methods tested showed errors due to long branch attraction under extreme conditions, maximum likelihood was by far the most successful in accurately resolving deep phylogenies.

Using protein parsimony long branch attraction already became a problem with modest differences in rate (ratio 1:3) and sequences that were about 50% identical, whereas maximum likelihood methods still performed well with realistic values of among site rate variation and branch lengths ratios of 1:12 (sequences less than 30% identical).

In the absence of fast evolving lineages (i.e., long branches were due to the absence of side branches only) all tested algorithms performed well even when sequences were below 20% identity,

and even when the alignment step was part of the reconstruction process. In contrast to findings obtained with nucleotide sequences, ASRV was found to facilitate phylogenetic reconstruction, especially if the alignment step is included.

ABUNDANT VIRUSES IN ANTARCTIC LAKES

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Perennially ice-covered Antarctic lakes exemplify microbially-dominated ecosystems existing at the extremes of conditions found on our planet. Viruses are the simplest, and conceivably most ancient, particles possessing the fundamental properties of living systems and may have been the original and/or only 'predators' near the dawn of life. It is now widely accepted that viruses are ubiquitous and abundant components of many extant aquatic ecosystems, where they are involved in gene transfer and may account for a significant fraction of microbial mortality. Current research is directed towards improving our understanding of forces operating on microbial evolution in early-Earth environments through the study of analogous systems.

In four of the lakes found in the McMurdo Dry Valleys, southern Victoria Land, Antarctica (i.e., Lakes Hoare, Fryxell, Bonney, and Joyce), planktonic, extracellular virus-like particles (VLPs) are plentiful. In two of these lakes, large, possibly novel icosahedral forms have been observed by transmission electron microscopy (TEM), and these viruses are morphologically similar to double-stranded DNA (dsDNA) viruses that are known to infect algae and protozoa but which have not been fully characterized. In one lake thus far examined, viruses also appear to have potentially high production potential. We summarize data on water column VLP distributions in four lakes collected during the 1995/96 and 1996/97 austral summer field seasons. Based on our data, we suggest that virally-mediated mortality may be a major biotic factor regulating the abundance of many of the microbes in these extreme environments. In addition, Antarctic lakes may constitute a large reservoir for undiscovered viruses possessing novel characteristics.

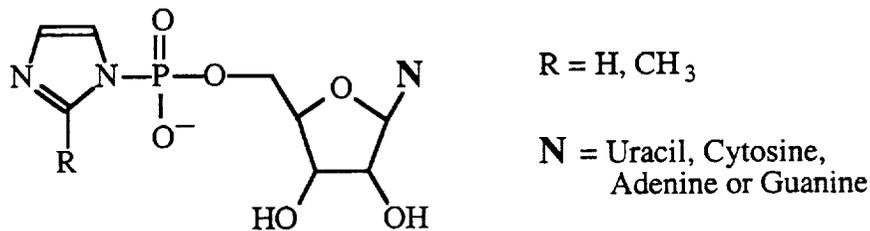
EFFECT OF LEAVING GROUP ON THE DIMERIZATION OF PHOSPHOIMIDAZOLIDE-ACTIVATED NUCLEOTIDES

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The discovery that RNA displays catalytic properties in conjunction with information transfer abilities has accelerated interest in RNA's role in the origins of life. For the RNA world hypothesis to be plausible, it is important to establish a mechanism for the non-enzymatic oligonucleotide synthesis. Before oligomerization can occur in any proposed mechanism, the initial steps must include the dimerization of monomers, and it is within this area that this study focuses upon. The broad goal of this project is to elucidate the factors that influence the dimerization process, thus presenting possible conditions where a substantial production of the internucleotide-linked dimers is viable.

Activated ribomononucleotides (see structure) are building blocks in non-enzymatic polynucleotide synthesis. In aqueous solutions, these substrates decompose to a variety of products, including nucleotide 5'-monophosphate (5'NMP) by cleavage of P-N bond and internucleotide-linked dimers (pNpN) by reaction of the ribose hydroxyl of one molecule with the P-N bond of another. Imidazole- and 2-methylimidazole-activated nucleotides were investigated, and the effects of these activating groups on the product distribution is the focus of this report. Not only does the leaving group have a dramatic effect on the relative product distributions of 5'NMP and pNpN, but it also influences the dimer distribution of pNpN and pyrophosphate-linked N5'ppN. More surprisingly, the pNpN dimers are significantly enhanced at the expense of N5'ppN with 2-methylimidazole when compared to imidazole.



HORIZONTAL GENE TRANSFER OF ARCHAEAL GENES INTO THE DEINOCOCCACEAE

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Members of the deep branching bacterial lineage Deinococcaceae (e.g. *Thermus* and *Deinococcus*) are classified as Bacteria based on cell wall and lipid composition, and ribosomal RNA sequence. In contrast, molecular phylogenetic analysis clearly shows that the catalytic and non-catalytic ATPase subunits found in *Thermus thermophilus* and *Deinococcus radiodurans* are archaeal or vacuolar type (A/V-ATPases). The best explanation for the presence of the A/V-type ATPase operon in *Thermus* and *Deinococcus* is horizontal gene transfer from the archaeal/eukaryotic lineage into the base of this bacterial lineage. Evidence which supports the transfer of other archaeal/eukaryotic genes into this lineage include:

- A *Thermus* prolyl tRNA synthetase fragment, first detected and isolated from a genomic library using a probe made against *Thermoplasma acidophilum* DNA, shows closest similarity to eukaryotic and archaeal homologues by BLASTX search.
- Both the *Thermus* prolyl tRNA synthetase fragment and its full length *Deinococcus* homologue (obtained from the TIGR database) group among archaeal and eukaryotic homologues with distance and quartet puzzling maximum likelihood methods.
- The next gene downstream from the A-ATPase operon of *Sulfolobus sulfotaricus* is prolyl tRNA synthetase (pers. comm., M. Ragan, D. Fague, Marine Resources Center, Halifax, NS)
- Although the data set is very complicated and suggests instances of paralogy, gene conversion and mis-assignment of function, malate dehydrogenase from *Thermus* and *Deinococcus* groups with other eukaryotic cytoplasmic MDH homologues rather than with the majority of bacterial sequences

Our findings indicate that these genes were horizontally transferred early in the evolution of the Deinococcaceae. The donating organism groups close to the root of the archaeal/eucaryal domains.

The transferred genes cannot be characterized by similar function, but their proximity in the *Sulfolobus* genome suggests that these genes might have been neighbors also in the genome of the donating organism.

**CHICXULUB IMPACT EJECTA IN BELIZE:
INSIGHTS INTO THE ROLE OF ATMOSPHERES AND VOLATILES
IN LARGE IMPACTS**

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Kevin O. Pope
Geo Eco Arc Research

Alfred G. Fischer
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John R. Marshall
SETI Institute

The mass extinction event at the Cretaceous/Tertiary boundary has been linked to the release of volatiles by the Chicxulub impact into the carbonate platform of northern Yucatan, Mexico. Chicxulub ejecta deposits in Belize provide the closest exposures of ejecta to the crater and the only known exposures of proximal ejecta deposited in a terrestrial environment. A quarry on Albion Island in northern Belize exposes ejecta deposits that are composed of a basal, ~1-m-thick clay and dolomite Spheroid Bed overlain by a ~15-m-thick coarse Diamictite Bed. Many and perhaps most of the clay spheroids are altered glass. Many dolomite spheroids have concentric layers and angular cores and are probably of accretionary lapilli origin. A slight iridium concentration (111–152 parts/trillion) was detected in the base of the Spheroid Bed. The Diamictite Bed contains ~10% altered glass, rare shocked quartz, 3-8 m diameter boulders, and striated and polished cobbles, one with a penetrating rock chip that plastically deformed the cobble. Chicxulub ejecta is exposed in several roadside quarries in the Cayo District of central Belize. Here, the upper surface of the Late Cretaceous carbonate platform is a highly irregular and extensively recrystallized horizon possibly representing deep karst weathering. Approximately 30 m of diamictite overlies this horizon with a texture similar to the Diamictite Bed at the Albion quarry, but with a more diverse lithology. In three locations the Cayo diamictites contain red clay layers with abundant polished and striated limestone pebbles and cobbles called Pook's Pebbles, several of which have penetrating rock chips and ablated surfaces.

We interpret the Albion Spheroid Bed as a deposit from the impact vapor plume that entrained fine debris from the ejecta curtain, but may also contain carbonate vapor condensates. The Albion and Cayo diamictites are the result of a turbulent flow induced by the interaction between the ejecta curtain and the atmosphere. The polished, striated, and ablated Pook's Pebbles are interpreted as high altitude ballistic ejecta that were partially melted upon reentry through the atmosphere. The Belize deposits provide valuable information on vapor plume dynamics and ejecta-atmosphere interactions that can be used to constrain impact models. They are also important for interpreting ejecta on other planets, especially the fluidized ejecta blankets on Mars, which may be a good analogue for the Belize ejecta deposits.

THE PHYLOGENETIC POSITION OF THE MICROSPORIDIA: DEATH OF AN EARLY BRANCHING LINEAGE?

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Phylogenetic analyses based on small subunit (SSU) ribosomal RNA sequences consistently group certain unicellular amitochondriate eukaryotes at the base of the eukaryotic lineage. These include the diplomonads, microsporidia and trichomonads and these organisms are believed to represent extant relatives of the oldest eukaryotes. The exact branching order of these lineages, however, is not consistent in all analyses and changes depend on which types of analyses are run and which organisms are included. Recently, the phylogenetic position of microsporidia has been called into question. Although SSU rRNA analyses suggest that these organisms are perhaps the most basal eukaryotic lineage, recent evidence, including phylogenetic analyses of β -tubulin sequences, heat shock proteins, RNA polymerases and reassessment of their meiotic life cycle, suggests that microsporidia may be most closely related to the fungi (for a recent summary see M. Mueller, "What are the *Microsporidia*?" Parasitology Today, in press, Oct. 1997).

Using vacuolar and archaeal type ATPase catalytic subunits we show that for this molecular marker the placement of the microsporidia at the bottom of the eukaryotic domain is not based on strong phylogenetic evidence. In agreement with SSU rRNA data distance analysis places *Nosema* on a long branch toward the base of the eukaryotic lineage, although the diplomonad *Giardia* remains the deepest eukaryotic branch. The deep branching is supported through bootstrap analyses; however, comparative analysis of alternative tree topologies employing maximum likelihood ratio tests indicates that the deep placement of the Microsporidia might be an artifact due to long branch attraction and peculiar substitution patterns in this lineage. Note that the same type of test provides strong support for the earlier branching of *Giardia*. In contrast, using maximum likelihood ratio testing on SSU rRNA phylogenies the placement of the microsporidia in the eukaryotic crown group together with fungi is significantly less likely than the deeper branching of the microsporidia. However, when the placement of the branch leading to the microsporidia is varied, the placement with the fungi corresponds to a local maximum of likelihood, suggesting that SSU rRNA and the different protein based phylogenies reflect the same evolutionary history. The contradiction between the different molecular phylogenies apparently is not due to a horizontal gene transfer of some protein encoding genes from higher eukaryotes into the microsporidia.

METABOLIC ACTIVITY OF MICROORGANISMS IN PERMAFROST

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The presence of significant numbers of bacteria in 3-5 million year old permafrost in North Polar regions and, according to recent findings, in Antarctica poses the question whether these organisms are in a state of "anabiosis" or are metabolically active. Although several reports of such activity at subzero temperatures exists in literature, quantitative studies have been lacking. The temperature of permafrost in N.E. Siberia is around -10° C while in the Antarctic McMurdo Dry Valleys region it varies between -18° C and -27° C.

We measured the incorporation of 14 C labeled acetate into lipids by bacteria in N.E. Siberian permafrost during an incubation period of 18 months at temperatures between $+5$ and -20° C. In thawed samples ($+5$ and 0° C) the labeled acetate was exhausted after 200-300 days. In frozen soil,

incorporation started after an over-one-month to six-months lag phase, increased until 200-300 days and appeared to stabilize (became non-measurable by our methods) after about 300 days. After 18 months of incubation the incorporation of ^{14}C into lipids represented 1245, 472 and 50 cpm for samples at -1.5 , -5.0 , and -10°C and very low but measurable counts, several cpm over the zero point, at -15.0 and -20.0°C .

We conclude that metabolic activity in permafrost is possible until at least -20°C . After freezing, such activity stabilizes at a level which is very low, yet sufficient to ensure repair of cell damage due to radiation and racemization.

WHAT ARE THE CARRIERS OF THE UIRS? SINGLE PHOTON INFRARED EMISSION SPECTROSCOPY (SPIRES) OF UV-EXCITED PAHS

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Identification of the carriers of the UIR bands remains a central problem in astrophysics. The currently available data generally support the "PAH Model" for UIR production, although identification of any specific carrier molecules has not been accomplished.

We have developed a new experiment for addressing this problem. Simultaneous desorption and excitation of PAH molecules in a cryogenic vacuum chamber is followed by time resolved detection of the dispersed infrared fluorescence. The very weak transient signals are detected by a novel liquid helium cooled spectrometer featuring a single photon counting BIB array.

The entire UIR spectral region ($3\text{-}15\ \mu\text{m}$) was monitored for a variety of small to medium sized PAHs (naphthalene, phenanthrene, pyrene, perylene, coronene) as well as hetero-substituted/functionalized PAHs (2-methyl-naphthalene, 2-methyl-phenanthrene, phenanthridine, dibenzofuran). While a general resemblance to the UIR bands was noted, major discrepancies in wavelength and relative intensities of the observed bands indicate that none of these PAHs are major carriers of the UIRs.

Further experiments are in progress to test PAH ions as possible UIR carriers.

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**STABLE CARBON ISOTOPE COMPOSITION
OF CYANOBACTERIAL AND *CHLOROFLEXUS* BIOMARKERS
IN HOT SPRING MATS CONSTRUCTED BY
OXYGENIC AND/OR ANOXYGENIC PHOTOTROPHS**

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Marcel van der Meer and Jan de Leeuw

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Modern microbial mats are studied as analogs of stromatolites, the predominant surviving fossils of Precambrian microbial life. Mats which occur in hot springs are among the best-studied model systems—understanding them gives insight as to the composition, structure and function of microbial communities that might have once predominated Earth's biota, and consequently its biogeochemistry. Most modern mats, including those in hot spring, are constructed by cyanobacteria, which are thought to cross-feed photosynthate to co-occurring green non-sulfur bacteria resembling *Chloroflexus*. However, some geothermal mats are constructed solely by *Chloroflexus* in the absence of cyanobacteria. These are of particular evolutionary interest as *Chloroflexus*, being more primordial than cyanobacteria, might have constructed the earliest stromatolites. This would have direct implications on whether the occurrence of stromatolites indicates the availability of biogenic oxygen on Earth, since green non-sulfur bacteria do not produce oxygen during photosynthesis.

We hypothesized that the stable carbon isotope signatures of *Chloroflexus* biomarkers should be different when it is growing alone (i.e., photoautotrophically using its unique CO₂ fixation pathway) as compared to when it is cross-fed by cyanobacteria (i.e., photoheterotrophically; assuming that "you are what you eat," its isotopic signature should be controlled by the cyanobacterial Calvin Cycle). Isotope ratio monitoring-gas chromatography was used to compare the isotopic compositions of lipid biomarkers in *Chloroflexus* mats and cyanobacterial mats. *Chloroflexus* mats are found in sulfidic carbonate-rich springs in the Mammoth Terraces Group, Yellowstone National Park; cyanobacterial mats occur downstream in the same springs. *Chloroflexus* biomarkers in the *Chloroflexus* mats were isotopically heavier than were cyanobacterial biomarkers in the cyanobacterial mats, consistent with the predominance of different autotrophic pathways. *Chloroflexus* biomarkers in the cyanobacterial mats were isotopically lighter than in the *Chloroflexus* mats, but were still substantially heavier than expected if *Chloroflexus* were predominantly cross-fed photosynthate from cyanobacteria. We infer that *Chloroflexus* is growing mixotrophically in these cyanobacterial mats, with photoautotrophy possibly supported by small amounts of primary sulfide remaining above the mat, or by biogenic sulfide produced within the mats.

**MARTIAN PALEOLAKE SEDIMENTS AND TERRESTRIAL ANALOGS:
EXTANT AND EXTINCT ICE-COVERED LAKES**

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Desert Research Institute

Images of purported fluvial systems on Mars suggest that there must have existed downstream locations where water pooled (e.g. Valles Marineris, Margarifer Sinus, Ma'Adim Vallis/Gusev Crater system), and the sediment load deposited (i.e. lakes). As the martian climate cooled, ice-covered lakes probably persisted as viable liquid water habitats for a long period of time. For this reason, perennially ice-covered lakes found in the polar regions are considered excellent analogs of potential past martian environments. Our research has focused on defining these extreme terrestrial habitats,

and the deposits they leave behind so that future Mars missions will be better able to make inference from lacustrine deposits discovered.

In the McMurdo Dry Valleys of East Antarctica we are presently concentrating on the controls of isotopic signatures left in the lake and deltaic sediments of the perennially ice-covered lakes. This research has led to the discovery of a paleoproductivity signal in the sediments. Organic mats in highly productive (shallow) areas exhibit decreased fractionation of carbon isotopes due to a diffusion limitation. Deep water sediments exhibit a more standard RUBISCO fractionation. This relationship breaks down in regions of stream inflow where environmental variability appears to be enforcing some influence on fractionation. Our upcoming field season will focus on this phenomenon so that deltaic sediments can better be used to elucidate paleoenvironmental information.

In order to define the succession of perennially ice-covered lakes we have investigated lakes in the high Arctic that occasionally retain their ice cover through the summer, and have located an Antarctic-like perennially ice covered lake in the Canadian high Arctic. Future investigation of this lake will tell us about how standard the Antarctic perennially ice-covered lake communities are, at least on this planet. We have also initiated investigations of a new lake environment in the Antarctic. Lake Vida is one of the largest lakes in the dry valleys, yet was previously thought to be frozen solid. Our recent field investigations revealed this lake to have an ~19 m ice cover over a hypersaline water body of undetermined depth. Ice cores retrieved contain microbial mat throughout, and once thawed, heterotrophic and autotrophic microbes are metabolically active. Samples of the sub-ice brine have not yet been obtained. Further investigation of this lake type will define a new extreme environment, and answer questions about the fate of a lake community upon cold termination of the lake.

THE OXIDATIVE STRATIGRAPHY OF THE MARTIAN REGOLITH

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We explore the role of impact cratering on the redistribution of oxidized materials on the martian surface. Although oxidation probably results from diffusion of photochemically-produced odd-H and O species, a diffusion/reaction model cannot predict the oxidative stratigraphy of Mars because the stratigraphic column itself is not stable. Both impact cratering and aeolian redistribution stir the regolith, burying oxidized surfaces and exposing reduced material to the atmosphere. Recovery of reducing materials from below the oxidized zone of the martian regolith is contingent upon understanding the chemical process responsible for the oxidation and the physical processes that stir the regolith.

The cratering/oxidation model assumes that the regolith is completely oxidized through depth Z_c , below which it retains its reducing nature. The model uses the actual cratering size-frequency distribution to calculate regolith gardening.

The probability of being missed by an impact is the ratio of the total area to the area of the crater, and the probability of being missed by n impact craters of the same size is $(ratio)^n$. The probability of being struck at least once is then $1 - (ratio)^n$. The probability of being buried by ejecta is estimated by a similar ratio of areas. The relative areas excavated and buried are tracked continuously, and the relative abundance of oxidized material is tracked with depth. At small sizes, the number of impacts can be extremely high, and the probability of a random point being affected by n impacts approaches 1.

We have measured the lifetime of H_2O_2 on basaltic material at $215^\circ K$, and found it to be $\sim 10^5$ seconds; the corresponding extinction depth, Z_e is 7 mm. The oxidation profile of the regolith is shown in Figure 1, assuming that only the upper 7 mm of the regolith are actively oxidized, but that a cratering flux representative of the heaviest Noachian cratering has stirred the regolith. Because roughly the upper 100 m has been excavated and buried many times, all material has visited the upper 7 mm and been oxidized. Return of reducing materials requires penetration to depths of 200 m. In Figure 2, the cratering record of the Chryse region is used. Cratering is ineffective in mixing the regolith after the end of heavy bombardment. The onset of oxidizing atmospheric conditions needs to be determined to establish the oxidized depth of the martian regolith.

Fig. 1

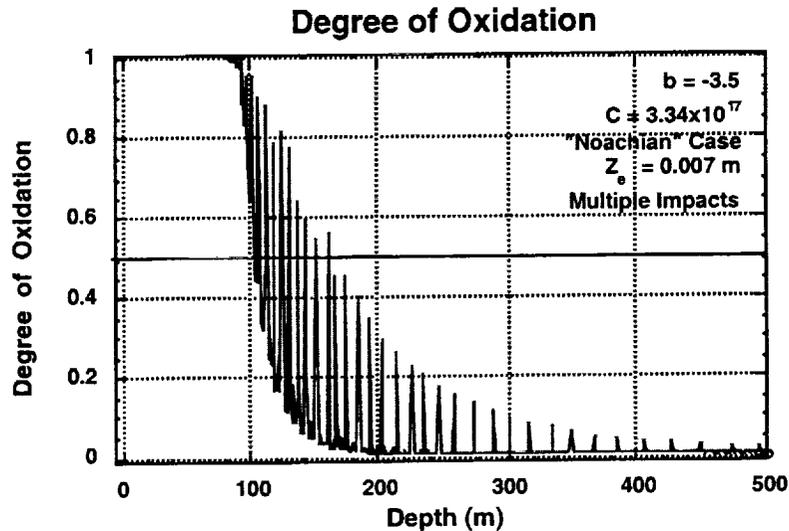
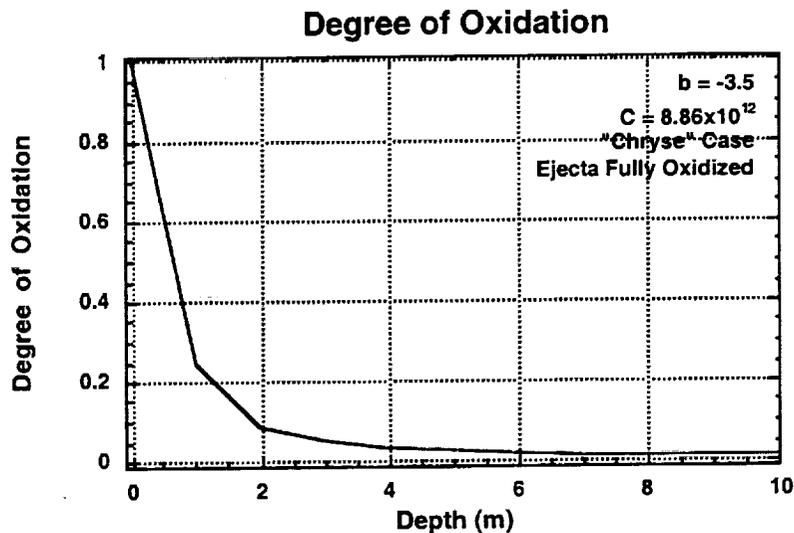


Fig. 2



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